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MECHANICAL REINFORCEMENT OF FILMS FROM RUBBER LATICES BY ADDED POLYMER PARTICLES

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by

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ABSTRACT

MECHANICAL REINFORCEMENT OF FILMS FROM RUBBER LATICES BY ADDED POLYMER PARTICLES

by

KOLAPO ALBERT POPOOLA

Various factors and filler characteristics which influence the ability of added polymer particles prepared as latices by emulsion polymerisation to reinforce the mechanical properties of films derived from rubber latices, particularly post-vulcanised natural rubber latex, have been investigated. The emphasis has been upon the enhancement of tear strength and puncture strength. The behaviour of polymer particles in latex films derived from other latices such as prevulcanised natural rubber latex, styrene-butadiene rubber latex and acrylonitrile-butadiene rubber latex, using particles which were expected to give optimum reinforcement on the basis of the principles which had emerged from the experiments on post-vulcanised natural rubber latex films, has also been investigated.

Various particle variables have been investigated. These include particle size, particle rigidity, particle glass-transition temperature, particle morphology and the nature of particle surface. The filler particles that have been used included polystyrene and polymethylmethacrylate particles of various sizes, crosslinked polystyrene particles, crosslinked polymethylmethacrylate particles, and polystyrene particles overcoated with polymers of long-chain acrylate/methacrylates and of VeoVa 10, and polystyrene particles whose surfaces have been functionalised with allylmethacrylate and with isoprene units. The filler latices have been blended with the rubber latices. Films have been obtained from the compounded latices by coagulant dipping in most cases, and then vulcanised. Electron micrographs have shown excellent dispersion of the individual filler particles in the rubber matrix.

The mechanical properties of the latex films have been determined. The enhancement of mechanical strength, particularly tear strength and puncture strength, observed in post-vulcanised natural rubber latex films has been attributed to such factors as the small size of the filler particle, the rigidity of the filler particle and strong physical and chemical adhesion between the filler particles and the rubber matrix. The tearing of the filled post-vulcanised natural rubber latex films proceeded in a knotty or stick-slip manner to leave rough irregular torn surfaces.

No significant reinforcement of the tear strength and puncture strength of the films derived from the other rubber latices has been observed. Possible reasons for this are discussed.

Advanced studies undertaken in connection with the programme of research in partial fulfilment of the requirements of the degree:

1. A course of postgraduate lectures and tutorials on surface chemistry, colloid science and emulsion polymerisation.

2. A course of guided study on the reinforcement of elastomers by particulate fillers.

3. A symposium organised by Plastics and Rubber Institute on 21st and 22nd May 1985, entitled "Polymer latex II".

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I am grateful to the Federal Government of Nigeria for the award of a Postgraduate Scholarship to carry out this work.

Last, but not least, I am most grateful to my wife, Funmi, for the inspiration she has given me.

CONTENTS

LIST OF ABBREVIATIONS

The following abbreviations have been used in this thesis:

NR	Natural rubber
LA	low ammonia (latex)
SBR	styrene-butadiene rubber
PS	polystyrene
PMMA	polymethylmethacrylate
PAcN	polyacenaphthylene
PαMS	polyα-methylstyrene
PBA	polybutylacrylate
PDA	polydodecylacrylate
PDMA	polydodecylmethacrylate
POMA	polyoctadecylmethacrylate
PVV10	polyVeoVa 10
PAMA	polyallylmethacrylate
PI	polyisoprene
CON	conventional (emulsion polymerisation)
SH	shot-growth (emulsion polymerisation)
SE	seeded-growth (emulsion polymerisation)
INV	inverse (emulsion polymerisation)
ZDC	zinc diethyldithiocarbamate
SAF	super abrasion furnace (carbon black)
pphr	parts per hundred of rubber
ppm	parts per million
pphm	parts per hundred of monomer
T_g	glass-transition temperature
LRC	London Rubber Company

CHAPTER ONE : INTRODUCTION

1.1 Concept of reinforcement of rubber

The concept of the term "reinforcement" arises basically in connection with composites built from two or more structural elements or components of different mechanical characteristics whereby the strength of one of these elements is imparted to the composite and combined with the set of favourable properties of the other components. An example is concrete strengthened with iron bars or steel rods embedded in it. The rods are bonded together by the high viscous concrete and overlap each other over a large proportion of their length. In this way, the high strength of the steel is imparted to the concrete to give it increased flexural and impact strength.

In the rubber industry, a different mechanism must be responsible for the reinforcement imparted to elastomers by particulate solids, because the solids are not so strongly anisometric that they can be said to overlap each other over large proportions of their length, nor are they actually so strong that they would be expected to impart additional strength to the composite. A clear definition of the term "reinforcement" as it is used in the rubber industry is therefore desirable.

Unfortunately, the term "reinforcement" as it is applied in the rubber industry is rather ill-defined. In 1920, Wiegand (1) suggested that the criterion for reinforcement is the energy at rupture, known as "resilient energy". The energy at rupture can be obtained from the stress-strain curve and the elongation axis. In 1938, Shepard, Street and Park (2) pointed out that tearing also must be taken into account in any adequate definition of reinforcement. The three authors also stated that "one of the most important effects of the addition of powders to rubber is the increase of abrasion resistance".

The same authors acknowledged the fact that these properties were difficult to measure accurately, especially in those days. Improvements in methods of measuring tear strength and abrasion resistance have shown that high values of these properties are not necessarily obtained either when the tensile strength is high or when the work of extension is high. Parkinson (3) describes reinforcement as follows : "reinforcement implies the incorporation into rubber of substance having small particles which give to the vulcanisate high abrasion resistance, high tear strength, high tensile strength and some increase in stiffness". Scott (4) and Payne (5) held the same view. A practical definition of reinforcement, which in my opinion emphasises the most important aspect of reinforcement, is the enhancement of mechanical properties that will lead to an improvement in the service life of a rubber article.

1.2 Reinforcement of dry rubber

The addition of particulate fillers to rubber is almost as old as the rubber industry itself. The effect of the known reinforcing fillers such as carbon blacks of various types and colloidal silicas on rubber vulcanisates is extremely important industrially. Other reinforcing fillers of special interest include colloidal clays, calcium silicate and various metal oxides. Certain resins, such as high styrene resins and crosslinkable phenolic resins, can also increase the strentgth of vulcanised rubber. The reinforcing effect of these fillers has been variously ascribed to the fine particle size as well as to physical and chemical interactions at the polymer-filler interface (6-9).

1.3 Reinforcement of rubbers in latex form

Mechanical reinforcement of rubbers in latex form by the use of spherical rigid polymeric fillers prepared as

latices by emulsion polymerisation has been of interest in recent years (9-13). The polymeric fillers used have included polystyrene, polymethylmethacrylate, polyacenaphthylene, polyacrylic/methacrylic esters, and various vinyl copolymers and terpolymers. In these investigations, the polymeric fillers were introduced by latex blending. In most cases, the blends were further compounded and coagulated, and vulcanised sheets were then prepared from the coagulum. As with the reinforcement of rubber vulcanisates by carbon blacks, such reinforcement of mechanical strength observed in materials prepared in this way has been variously ascribed to such factors as the small size of the filler particles, the rigidity of the filler particles, and strong physical adhesion between the filler particles and the rubber matrix. Chemical bonding between the filler particles and the rubber matrix seems to have little effect upon reinforcement.

More recently, there has been interest in the possibility of reinforcing by polymeric fillers films which are obtained directly from rubber latices by processes such as casting and dipping (14-16). The emphasis has been upon mechanical properties such as tear strength and puncture strength, rather than upon tensile strength and modulus. Indeed, for some applications, what is required is enhancement of tear strength and punture strength without significant increase in stiffness.

1.4 Aim and plan of the present work

The main aim of this project was to investigate the factors which influence the ability of added polymer particles, prepared as latices by emulsion polymerisation, to reinforce the mechanical properties of vulcanised films derived from rubber latices. In particular, the investigation was to be concerned with the effects of particle size, particle nature, particle structure and particle surface upon ability to reinforce post-vulcanised films from natural rubber latex. It was also proposed that

experiments should be carried out with other types of latex, such as prevulcanised natural rubber latex, styrene-butadiene rubber latex, and acrylonitrile-butadiene rubber latex, using particles which would be expected to give optimum reinforcement on the basis of principles which emerged from the experiments on post-vulcanised natural rubber latex films. Most of the previous work on this subject has been empirical in nature, and little so far has emerged concerning the principles which underlie the reinforcement of rubber films produced in this way. A detailed investigation of these principles was therefore appropriate.

It is hoped that, as a result of the present work, a deeper understanding than hitherto will be gained concerning the behaviour of polymeric fillers in thin rubber films. The results of the investigation could be of significance for the manufacturer of thin rubber articles, such as gloves and condoms. The common form of failure of rubber gloves is the formation of a hole or a slit in the rubber caused by the penetration of a sharp object from outside, such as a knife, or from the inside by a sharp finger-nail. There is, therefore, the need to improve the tear strength and puncture strength of rubber gloves, without increasing the stiffness or decreasing the extensibility of the product. With the advent of AIDS, it has become desirable that condoms should have higher tear strength and puncture strength than hitherto.

In order to study the reinforcement of films from rubber latices by added polymer particles, various particle variables are available for investigation. These include :

I) particle size
II) particle rigidity
III) particle glass-transition temperature
IV) particle morphology
V) particle surface

The present programme was designed to investigate these variables.

In order to acheive the main objective of the investigation the experiments that were carried out were divided into two phases. Most of the work comprised the first phase.

I. An initial phase, in which a broad survey of the effects of various rigid polymeric fillers upon the mechanical properties of post-vulcanised films derived from natural rubber latex was carried out. The polymeric fillers investigated were :

a) polystyrene particles of various sizes, as an example of rigid non-polar particles;
b) polymethylmethacrylate particles of various sizes, as an example of rigid polymer particles of somewhat greater polarity than polystyrene;
c) crosslinked polystyrene particles and crosslinked polymethylmethacrylate particles, to see if crosslinking the rigid particles affects their ability to modify the mechanical properties of post-vulcanised natural rubber latex films;
d) polyacenaphthylene particles, as an example of rigid polymer particles of high glass-transition temperature, well above the temperature at which the rubber was vulcanised.

In this phase, a broad survey of the effects of copolymerising the monomer of the "rigid" polymeric filler with a "plasticising" monomer in various ways was also carried out. Also investigated was the possibility of enhancing the level of reinforcement by promoting interaction between the surface of the filler particles and the rubber matrix in which they are embedded. In this part of the investigation, several matters have been investigated, including

I) the effect of reducing the glass-transition

temperature of polystyrene particles by copolymerising with butylacrylate - a "plasticising" comonomer

II) the effect of particle morphology (random, core-shell, etc.) of a styrene/butylacrylate copolymer particle, keeping overall composition constant;

III) the effect of varying the alkyl chain length, and hence tendency to mix with rubber, of the alkyl acrylate/methacrylate comonomer; the use of the "speciality" monomer, VeoVa 10, was also investigated;

IV) the effect of using a "linking" monomer to bond the shell to the core covalently in the case of core-shell copolymer particles;

V) the effect of introducing co-vulcanisable groups into the surface of core-shell particles using allylmethacrylate and isoprene units.

II. In the second phase, an investigation was made of the behaviour of polymeric filler particles in latex films derived from other rubber latices. The rubber latices that have been briefly investigated include prevulcanised natural rubber latex, styrene-butadiene rubber latex, and acrylonitrile-butadiene rubber latex. The particles that were used in these experiments were those that were expected to give optimum reinforcement on the basis of principles which emerged from the experiments on post-vulcanised natural rubber latex films.

CHAPTER 2 : SURVEY OF LITERATURE PERTAINING TO FILLER CHARACTERISTICS, THEORIES OF REINFORCEMENT AND FILM FORMATION FROM LATICES

2.1 Factors and filler characteristics influencing reinforcement of rubber vulcanisates

During the recent years, various studies have been carried out on the characteristics of particulate fillers that influence the properties of filled rubber vulcanisates. The well-known effects of reinforcing fillers such as carbon black and silica in enhancing the strength of vulcanised elastomers has been variously ascribed to the fine particle size as well as to the physical and chemical interactions at the polymer-filler interface (1- 4). Similarly, various studies (5-9) carried out on the reinforcement of natural rubber and styrene-butadiene rubber by added polymer particles indicate that the reinforcement of such vulcanisates is affected by the particle size and modulus of the filler, as well as by degree of adhesion between the filler particle and the matrix. Although some of these factors have been extensively investigated, the complexity of the problem involved in elucidating the mechanism has made it difficult to evaluate the significance of each factor. However, several attempts have been made to separate the contributions made by them.

2.1.1 Concentration of filler

Generally, with increasing concentration of filler in the rubber, all the strength properties pass through a maximum for moderate concentrations of fillers, with the exception of stiffness which increases continuously (10-12). Figures 2.1 and 2.2 illustrate the effect of concentration of carbon black upon various mechanical

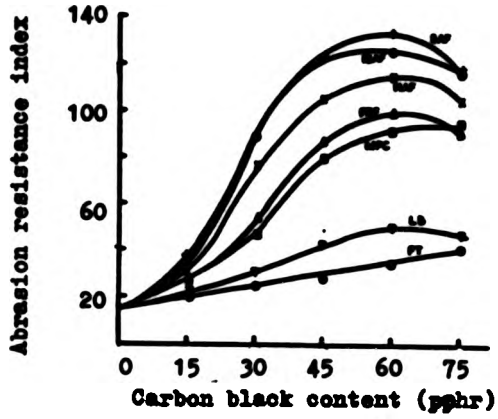


Fig. 2.1 Effect of carbon black concentration upon abrasion resistance of NR vulcanisates(10)

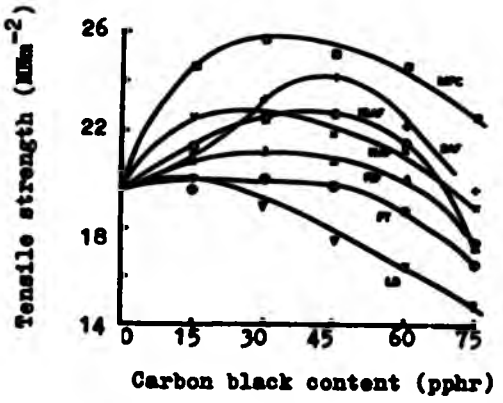


Fig. 2.2 Effect of carbon black concentration upon tensile strength of NR vulcanisates(10)

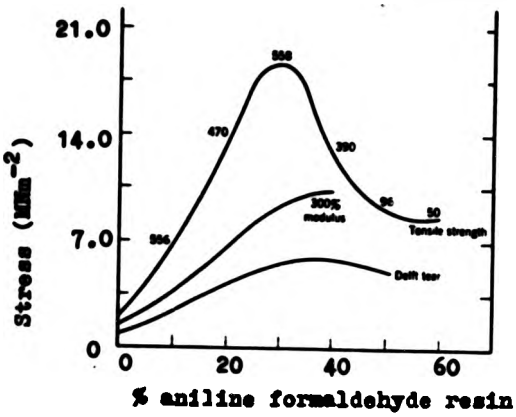


Fig. 2.3 Effect of resin concentration upon the mechanical properties of SBR vulcanisates. Numbers on tensile curve represent ultimate elongation (12)

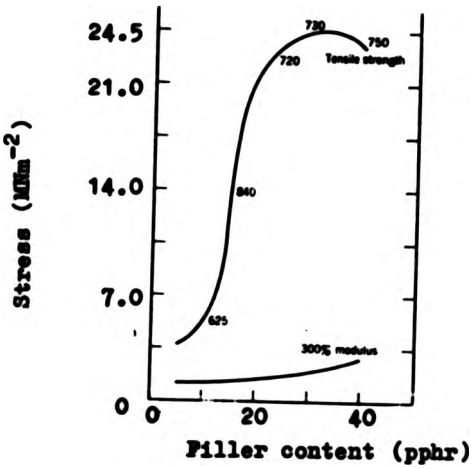


Fig. 2.4 Effect of polystyrene/polymethacrylate/ polydivinylbenzene (80/10/10) loading upon SBR vulcanisate properties. Numbers on tensile curve represent ultimate elongation (12)

properties. Figures 2.3 and 2.4 show the effects of aniline formaldehyde resin and styrene/methacrylate/divinylbenzene (80/10/10) terpolymer particles upon the mechanical properties of styrene-butadiene rubber vulcanisate.

What determines why this maximum occurs is unknown. Weigand (11) has suggested that these maxima represent limits to the quantity of filler which can be closely associated with rubber.

2.1.2 Size and shape of filler particles

As has been remarked above, small particle size has long been recognised as a necessary prerequisite for the manifestation of reinforcement in a filled rubber vulcanisate. Several studies have been carried out in order to demonstrate the contribution towards reinforcement made by filler particle size. Only a few of these studies have provided quantitative evidence concerning the magnitude of the particle-size effect.

2.1.2.1 Carbon black and non-black mineral reinforcing fillers

The work of Alter (13) represents an attempt to provide quantitative correlations between filler particle size and change in various mechanical properties of polymer-filler blends. Alter presented data for the effect of mineral fillers such as silicas, silicates, alumina and calcium carbonate, on the mechanical properties of polyethylene, styrene-butadiene rubber, and natural rubber. Rubber-carbon black systems were omitted because of the belief that specific chemical interaction might seriously obscure the relationship being sought. Alter tested the dependence of mechanical properties of the vulcanisates, such as modulus and yield strength, by plotting the values of the relative modulus (modulus of filled polymer/modulus of unfilled polymer) and relative

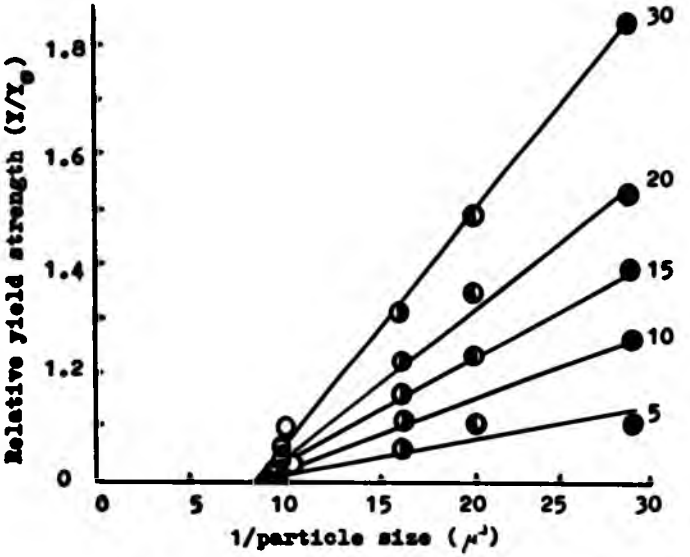


Fig. 2.5 Relative yield strength of polyethylene containing various fillers at the indicated volume percent loadings vs. reciprocal of filler diameter: ○ aluminium hydrate C-741, ⊖ calcium carbonate, ◑ calcium silicate, ◐ precipitated silica, ● amorphous silica (13)

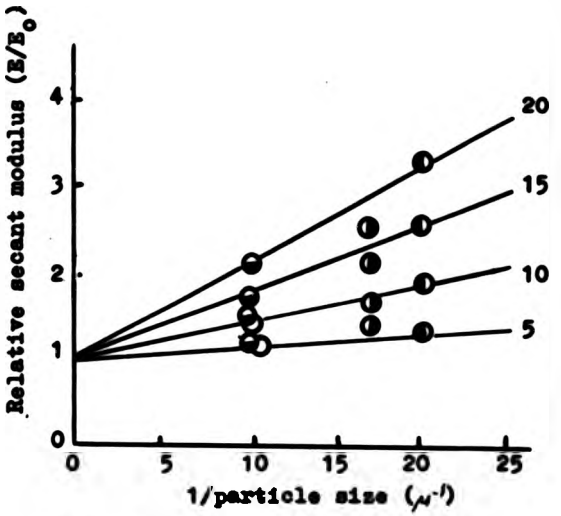


Fig. 2.6 Relative secant modulus vs. reciprocal of filler diameter for filled polyethylene. Symbols same as in title of Fig. 2.5 (13)

yield strength (yield strength of filled polymer/yield strength of unfilled polymer) against the reciprocal of filler particle diameter. To a reasonable approximation, the mechanical properties of the filled polymers were found to vary linearly with the reciprocal of the filler particle diameter. Two of the several plots are shown in Figures 2.5 and 2.6. The importance of particle size for any single filled polymer system clearly emerges from this study.

Oberth (14) carried out work on the effect of particle size and shape upon the mechanical properties of polyurethane vulcanisates containing both organic and inorganic fillers. Some of the fillers used and the mechanical properties of the filled vulcanisate determined are given in Table 2.1. Figures 2.7 and 2.8 demonstrate the effect of particle size upon tensile stress-stain curve at low and high filler loadings respectively. Oberth concluded that strength reinforcement depended strongly upon particle size and also upon additional factors such as stress concentration brought about by filler particles, and that stress concentration itself is a function of shape, volume fraction of filler, and arrangement, as well as particle size distribution of the dispersed phase. He also concluded that the enhancement of the initial tensile modulus (Young's modulus) is independent of particle size. It should be noted that the conclusion reached by Oberth regarding the effect of particle size upon initial modulus is contrary to the network theories of filler reinforcement (1,15). However, there is ample evidence in the literature that supports the view that initial modulus is independent of particle size. For example, Cohan (16) investigated calcium carbonate fillers as well as carbon black and found no effect of particle size upon initial modulus. In a review on filled elastomeric systems, Payne (17) lists overwhelming evidence for the independence of initial modulus upon particle size.

Table 2.1 Effect of 10 vol-% of selected fillers upon tensile properties of a polyurethane rubber (14)

Filler	Young's modulus MNm^{-2}	Ultimate stress MNm^{-2}	Ultimate strain	Particle size and shape μ
None	1.04	0.75	1.50	-
Carbon black	1.51	1.29	2.93	Spherical 0.2
Fe_2O_3	1.60	1.33	2.81	Spherical 0.18
Glass	1.49	0.70	1.65	Spherical 10
Polystyrene	1.44	0.69	1.10	Spherical 40
Polystyrene	1.40	0.57	0.75	Spherical 200
Polystyrene	1.42	0.35	0.50	Spherical 2000
Al(E-15)	1.51	1.04	1.45	Spherical
Al platelets	4.18	0.55	0.23	Platelets 0.635 x 0.635 x 0.013 mm

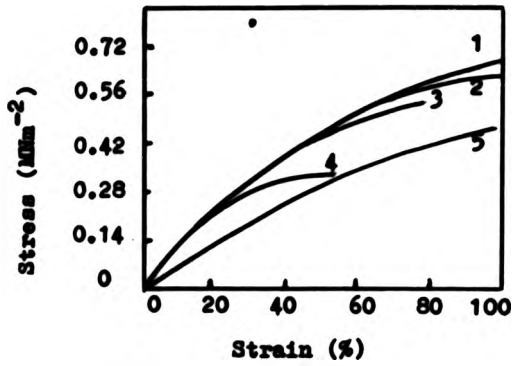


Fig. 2.7 Effect of particle size upon tensile stress-strain curve of filled polyurethane rubber. Filler content: 10% by volume; 1,carbon black-0.2μ; 2-4,polystyrene - 40, 200, 2000μ ; 5 is unfilled vulcanisate (14)

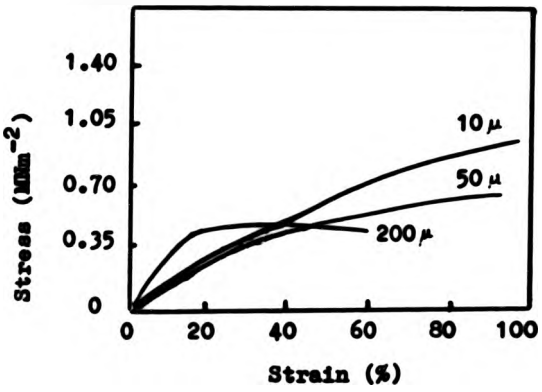


Fig. 2.8 Effect of particle size of glass spheres upon tensile stress-strain curve of filled polyurethane rubber. Filler content: 60% by volume; numbers appended to curve indicate particle diameter (14)

2.1.2.2 Polymeric fillers

Morton et al. (6-9) carried out several studies on the effects of the particle size of polymeric particulate fillers such as polystyrene, polymethylmethacrylate and a 90/10 styrene/butadiene copolymer upon the mechanical properties of elastomers such as natural rubber and styrene-butadiene rubber. The polymeric fillers were prepared by emulsion polymerisation. The filler-elastomer mixtures were prepared by blending the rubber and the filler as latices, and then coagulating the compounded latex mixture. Vulcanised sheets were then prepared from the coagulum by vulcanisation at 60°C. Figures 2.9 and 2.10 demonstrate the effect of filler particle size upon the extent of reinforcement. The tensile strength is denoted by σ_b whilst t_b and a_T denote the time to break and shift factor respectively. It can be seen that a decrease in particle size increases the tensile strength of the vulcanisate at any given strain rate and temperature.

Burke (12) has also carried out work on the effect of particle size upon the reinforcement of styrene-butadiene rubber by polymeric fillers. He prepared a series of colloidal-sized styrene/divinylbenzene/acrylonitrile (75/20/5) terpolymer particles having average sizes in the range 25 - 650 nm. Those having particle sizes in the range 25 - 50 nm were found to be reinforcing, but fillers having large particle sizes were not. Figure 2.11 clearly demonstrates this effect.

Although the enhancement of strength by particulate fillers is believed to depend upon particle size of filler, there is as yet no satisfactory mechanism to explain this effect. Oberth (14) and Nielsen (18) have proposed that the increase in interfacial area per unit volume of filler as particle size decreases must be an important factor in accounting for the lack of dependence of Young's modulus upon particle size and the increase of tensile strength of filled system with decreasing particle

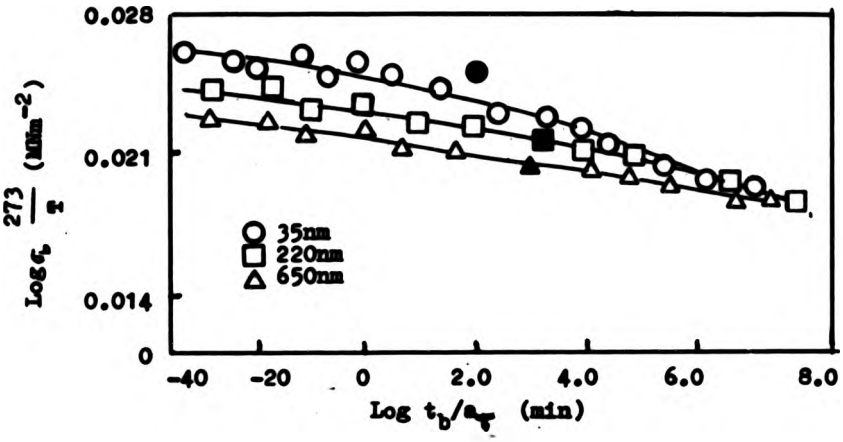


Fig. 2.9 Effect of polystyrene particle size upon tensile strength of SBR vulcanisates. Filled points refer to tensile strength determined at 25°C and 500mm/min strain rate (6)

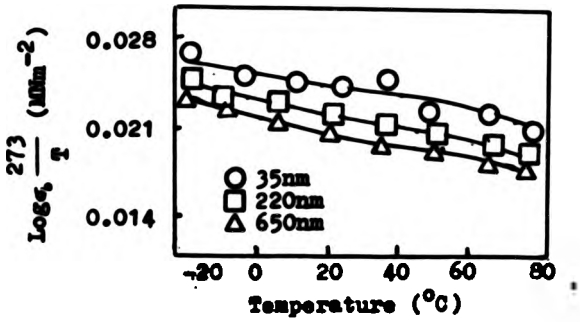


Fig. 2.10 Effect of polystyrene particle size upon tensile strength of SBR vulcanisates at various temperatures. Strain rate - 500mm/min (6)

size of filler. These authors have also suggested that the independence of the stress fields near the particle upon the size of the particle may also be important. However, they accept that the reason for the dependence of the enhancement of strength by particulate fillers upon the particle size of the filler is not entirely clear.

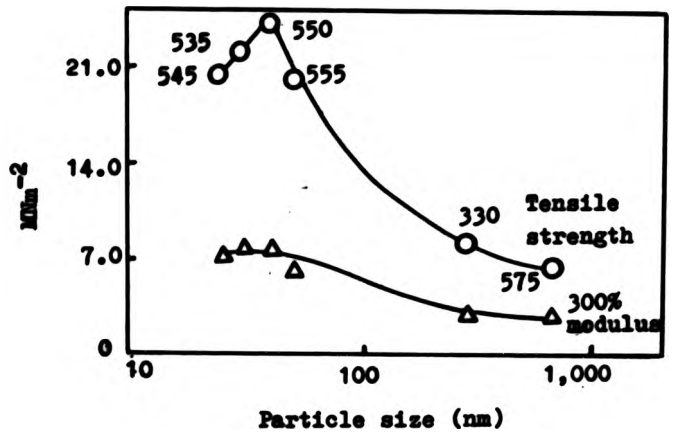


Fig. 2.11 Effect of particle size upon reinforcement of SBR by styrene/divinybenzene/acrylonitrile (75/20/5) terpolymer particles. Filler loading - 50 pphr; numbers on tensile curve represent ultimate elongation (12)

2.1.3 Nature of filler surface

Since for a given specific surface area, particles of different substances reinforce to different extents, it has long been considered that the reinforcing of composite systems is influenced by the nature of filler surface as well as by the size of the particle (5,6,19-50). It used to be thought that the reinforcing effect of carbon blacks was due primarily to the size and spherical shape of the particles. However, subsequent comparisons with non-black filler having particles of similar size and shape suggest

that carbon black particles have some other property, such as ability to interact with the rubber matrix, besides size and spherical shape which makes them particularly effective as reinforcing agents. Different views are held by various workers as regards the nature of the interaction in many systems, and also upon relative importance of each type of interaction upon the mechanical properties of the composites. There is ample evidence in the literature for both physical (5,6,19,48-50) and chemical (21-40) interactions, especially in the case of rubber filled with carbon black.

In the present section, evidence for both chemical and physical interactions between rubber and particulate carbon black filler and between rubber and particulate polymeric filler is discussed. However, it is important to note that it is not sufficient to know the nature of these interactions or of any bonds which may be present as a consequence; it is also necessary to demonstrate that such interactions actually contribute to reinforcement. In this connection, this section also discusses the attempts which have been made to show the relevance of such interactions to the mechanism of reinforcement of rubbers by particulate fillers.

2.1.3.1 Chemical interaction between filler and matrix

Chemical bonding between filler and rubber in the conventional explanation of the phenomenon of "bound rubber", has been regarded as an important factor for the reinforcement of rubber by many authors. The term "bound rubber" was first used by Fielding (32). It refers to all the rubber in unvulcanised filled rubber stocks which is insoluble in benzene. The actual mechanism of this phenomenon is far from clear. The signicance of this phenomenon for the particulate reinforcement of rubber is also obscure.

(A) Chemical interaction between rubber and carbon black, and between rubbers and non-black mineral fillers

The work of Rehner (3), of Garten and Sutherland (29). of Gessler (37) and of Whorlow (38) among others indicates that some type of chemical interaction between rubber and carbon occurs. More than one type of reaction has been suggested.

A chemical bond resulting from linkages of carbon black to rubber through reaction with sulphur molecules was postulated by Naunton and Waring (39). The formation of such a type of carbon-to-rubber crosslink might be expected to occur via chemical unsaturation at the filler surface as well as in the polymer molecules.

The view of Naunton and Waring was supported by Stearns and Johnson (40) whose work on the heats of reaction of bromine with reinforcing carbon blacks have led them to postulate the presence of double bonds on the carbon black surface and the formation of linkages to rubber through reaction with sulphur molecules. However, their evidence for the presence of double bonds on the carbon blacks is not conclusive, because similar heats of reaction do not necessarily imply similar types of chemical entity. Their mechanism is also incompatible with the fact that carbon blacks strongly reinforce polychloroprene rubber which does not require sulphur for vulcanisation. In addition, they did not test their theory by measuring the reinforcing ability of the brominated blacks.

In contrast to the findings of Naunton, Waring, Stearns and Johnson, extensive investigation (38-46,50) into the surface activity of different types of carbon blacks have shown that unsaturation in carbon blacks is unlikely to be a factor in promoting reinforcement of rubber vulcanisates. However, Pike and Watson (47) have shown that the formation of chemical linkages between carbon black and rubber does not necessarily involve unsaturation of the black. These authors have shown that

during cold milling of rubber which produces chain scission, the ruptured polymeric chains are free radicals. It has been argued by Watson (35) and Garten and Sutherland (29) that reinforcement results from the chemical attachment to ruptured rubber molecules to carbon black particles, the latter acting as radical acceptors for the ruptured rubber molecules. Experiments on cold milling reported by Watson (35) showed that the amount of carbon-rubber gel (or bound rubber) increased with time of milling of rubber and carbon black in air to a maximum depending upon the grade of carbon black. Only the stress-strain properties of the rubber-black vulcanisates were examined. Modulus was shown to be at maximum after light milling when the gel content was also at a maximum, a decrease in modulus being observed with further milling. Watson suggested that the preliminary increase followed by a decrease in modulus with further milling is a free end effect. Watson pointed out that, if his proposed mechanism for gel formation is correct, the gel content should be reduced by addition of a radical acceptor such as thiophenol or hydrazobenzene. He found this to be the case, the reduction being in the order expected from the efficiency of the radical-acceptor.

Watson has suggested the following mechanism for shear-induced formation of chemical linkages between rubber and carbon black, with the consequence formation of bound rubber :

P (polymer)	$\rightarrow$ R. + R.	scission of polymer molecule leading to formation of radical R. (initiation)
R. + R.	$\rightarrow$ R - R	radical recombination
R. + RX	$\rightarrow$ RX	termination by acceptor X

$2R. + F \longrightarrow R\text{-}F\text{-}R$ crosslink by filler acceptor F

However, in addition to the above reactions, one would expect other types of reaction which might lead to the formation of polymer-polymer crosslinks e.g.,

$R. + P \longrightarrow RH + P.$ hydrogen abstraction

$R. + P \longrightarrow R\text{-}P$ branching

$2P. \longrightarrow P\text{-}P$ polymer-polymer crosslink

Such reactions will also contribute to the apparent amount of bound rubber which is formed.

In view of the controversy over the relevance of carbon black unsaturation to reinforcement, the work of Watson and associates is particularly interesting in that they have shown that the formation of chemical linkages between carbon black and rubber which leads to improved physical properties of the filled vulcanisate does not necessarily involve unsaturation of carbon black. However, the nature of these linkages, and how they contribute to reinforcement, especially in the case of rubber containing carbon black particles remains a subject of controversy.

(B) Chemical interaction between rubbers and polymeric fillers

Extensive studies (6,9) have been carried out on the elastomer-polymeric filler chemical bonding and its effect upon reinforcement of the filled vulcanisates. These studies have so far shown that the presence of chemical bonds has no significant effect upon reinforcement.

Experiments with both polystyrene particles and styrene-butadiene coplymer particles as model fillers in styrene-butadiene rubber vulcanisates have been carried out by Morton, Healey and Denecour (6). In carefully-controlled experiments, they could show

that, in the case of the polystyrene particles, no chemical bonds were formed between the particles and the rubber matrix during vulcanisation; this was to be expected since the polystyrene chain molecule has no olefinic double bonds and hence is not reactive. By copolymerisation with 5-10% butadiene, chemical unsaturation was introduced into the molecular chain, and particles made from this copolymer showed evidence of being chemically bound to the rubber. The tensile strength of the various vulcanisates showed that filler-elastomer bonds have no effect upon reinforcement. This effect is well demonstrated in Figure 2.12 for styrene-butadiene rubber vulcanisate which contained polystyrene particles and styrene/butadiene (95/5) copolymer particles. The tensile strength is denoted by

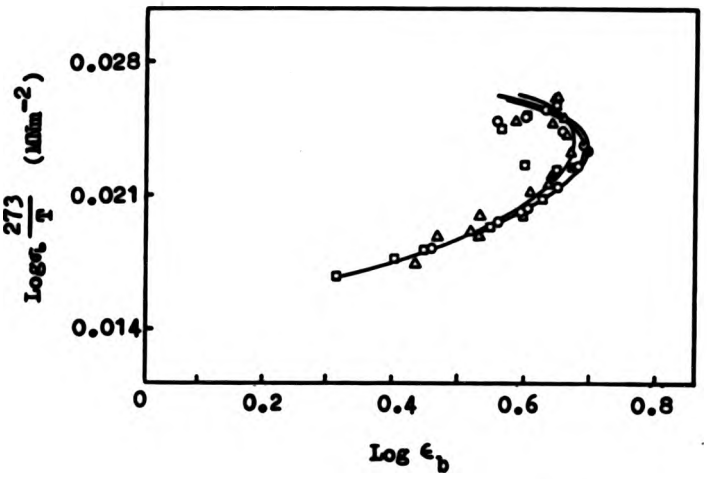


Fig. 2.12 Effect of filler-elastomer attachment on failure envelopes . ○ PS; □ SB-5; △ SB-10; ●,■,▲, refer to tests carried out at 25°C and 500 mm/min. Volume fraction of filler : 0.15 (16)

σ_b, and t_b and a_T denote the time to break and shift

factor respectively. In order to put the data in proper perspective, the tensile strength determined at normal test conditions, i.e., 25°C and 500 mm/min, are denoted by filled points in Figure 2.12. It can be seen that the presence of filler-elastomer bonds does not alter the failure envelope. These workers have concluded that although the filler-elastomer bonds are apparently exerting a slight effect upon the viscoelastic response, they are far too weak to affect the overall network density of the rubber.

It should be pointed out that, in the case of carbon black, the viscoelastic response of the network is also affected by the presence of the carbon black particles; but unlike polymeric filler particles, the crosslink density is increased. The evidence for the effect of carbon black upon viscoelastic properties is that the failure envelopes at different loadings do not superpose, showing a tendency to go to higher stress values at higher filler loadings (48).

2.1.3.2 Physical interaction between filler and matrix

As stated before, some investigators regarded the origin of adhesion between filler particles and rubber matrix as being essentially physical bonding, e.g., a type of labile adsorption.

(A) Physical interaction between rubbers and carbon black, and between rubbers and non-black mineral fillers

The extent of adsorption of styrene-butadiene rubber and butyl rubber on carbon blacks has been shown to be proportional to the surface area of the black, and to be independent of the chemical nature of the black (48). Gilliland and Gutoff (49) observed hysteresis in the adsorption of polyisobutylene and butyl rubber on various carbon blacks, but found that the adsorption was physical.

Frisch et al. (50) have studied the physical interaction between polystyrene and carbon black, and found that multiple physical contacts of chain segments exist between the polymer and the surface of filler.

Pierre and Chahal (19) have carried out a more quantitative investigation of the physical interactions between polymer and filler in which they have attempted to correlate the interfacial energies (measured in terms of heat of adsorption of silica/polydimethylsiloxane interfaces) with relaxation modulus of the silica/polydimethylsiloxane vulcanisates based on the same PDMS and silcas as were used in the adsorption experiments. The heat of adsorption of a model compound (octa-methlylcyclotetrasiloxane) on the filler surface was taken as a measure of the interfacial energy. They expected that the behaviour of the polymer towards the filler would be similar to that of the model compound. They have found that the relaxation moduli of the silica/polydimethylsiloxane vulcanisates increased with increasing heat of adsorption.

(B) Physical interactions between rubbers and polymeric fillers

As has been remarked above, the presence of chemical bonds between filler and rubber matrix has no significant effects upon reinforcement. However, further studies (9, 14) have shown that better adhesion between filler and rubber leads to higher strength. Morton et al. (9) prepared a series of polymethylmethacrylate and polystyrene latices by emulsion polymerisation. Two additional fillers were also prepared from polystyrene latex by modifying the particle surface with additional emulsifier (sodium oleate) in such a way as to give a fully soap-saturated particle surface and another which was not completely saturated. These two soap-modified polystyrene fillers are identified as 440(100%S) and 440(60%S) respectively in Figures 2.13 and 2.14. The

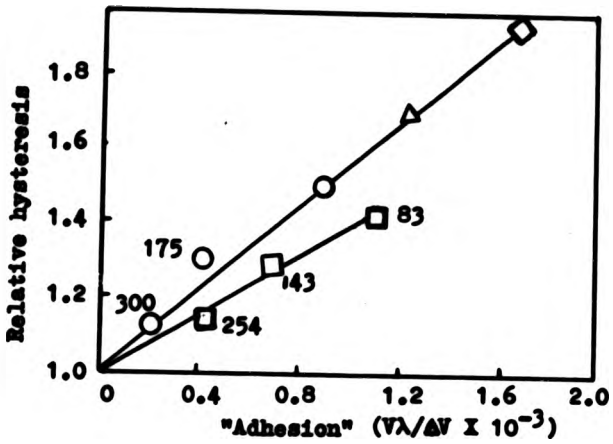


Fig. 2.13 Effect of filler-rubber adhesion upon relative hysteresis of filled SBR vulcanisates. Filler - 25 vol.%; ○ PS44; △ PS44(66% S); ◇ PS44 (100% S); □ PMMA; numbers adjacent to points are particle diameters in nm (9)

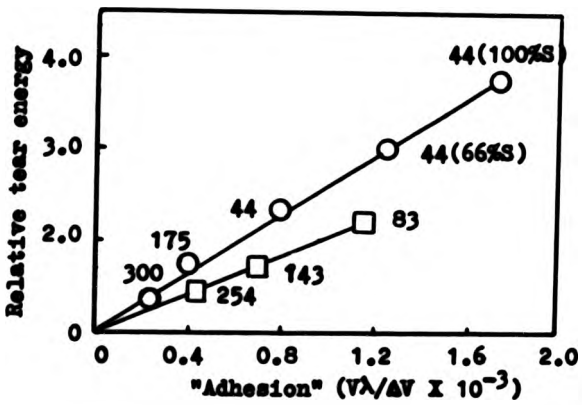


Fig. 2.14 Effect of filler-rubber adhesion upon tear strength of filled SBR vulcanisates. Filler-25 vol.%; numbers adjacent to points are particle diameters in nm (9)

effect of the adhesion difference on reinforcement of the vulcanisates was determined by measuring uniaxial stress-strain hysteresis as well as tear strength. The authors presumed that these characteristics are directly related to each other (51,52). Figures 2.13 and 2.14 illustrate the effects of filler-rubber adhesion upon the relative hysteresis and tear strength of the vulcanisates respectively. The filler-rubber adhesion was quantified by the reciprocal of the dilation parameter, $\Delta V/V\lambda$, where $\Delta V/V$ is the fractional volume at strain λ. The relative hysteresis is defined as the ratio of hysteresis of the filled vulcanisate to that of the gum vulcanisate. The tear strength was quantified by relative tearing energy as the ratio of tearing energy of the filled vulcanisate to that of the gum vulcanisate. It can be seen from these graphs that better adhesion gives better tear strength but higher hysteresis.

Morton et al. have proposed that the increase of hysteresis with increasing adhesion shows that the restriction imposed by the filler on the elastic response of the elastomer depends upon the degree of adhesion between the two. Thus the energy-absorbing characteristics of the filler are enhanced by improved filler-rubber adhesion. As they expected, the filler raises the tear energy in an analogous manner to its effect upon hysteresis, because these characteristics are presumably directly related to each other as remarked before.

2.1.3.3 Molecular slippage mechanism of reinforcement

Mechanisms of reinforcement involving molecular slippage have been proposed by various workers (1,53,54). They all agreed that under strain condition molecular segments can slip over the filler surface to accommodate stress, and undergo molecular alignment which contributes to increased strength.

This type of mechanism is based upon the assumption that rubber molecules are associated with the surface of

the filler particle, and that they can undergo molecular slippage under stress. As a consequence of this slippage, the applied stress is more uniformly distributed among the adsorbed molecules in the interfacial regions than hitherto. The shortest chain segments between particles are the first to reach the limit of finite extensibilty, beyond which rupture would occur if they were strained further. Their ability to permit the inter-particle distance to increase by a process of molecular slippage prevents their rupture and causes other neighbouring molecular chains of longer chain length between particles to bear an increased stress. More chains then effectively carry the load, and a higher strength results.

A schematic illustration of reinforcement by slippage mechanism is shown in Figure 2.15. This shows three chains of different lengths between two filler particles in the direction of applied stress. As the stretching proceeds from stage 1, the first chain slips at the points of connection A and A' until the second chain is also taut between B and B' (stage 2) and, when furher elongated, starts to slip there so that finally stage 3 is reached in which all the three chains are stretched to their maximum extent and share the imposed load equally. The resulting uniform distribution of stress between the chain gives the high improvement in strength. In stage 4. the tension is relieved and the material has retracted. The situation now is not the same as originally (stage 1), because, owing to the slippage, the three chains now have approximately equal lengths.

This mechanism appears quite significant in that it helps to explain some of the characteristic mechanical behaviour of reinforced vulcanisates. For instance, it explains the so called "Mullins effect" (stress softening) as repeated extension will now develop a lower modulus than was developed during the first cycle, because the energy of slippage does not now have to be provided, as it was during the first cycle. According to this mechanism, part of the elastic modulus which is developed during the

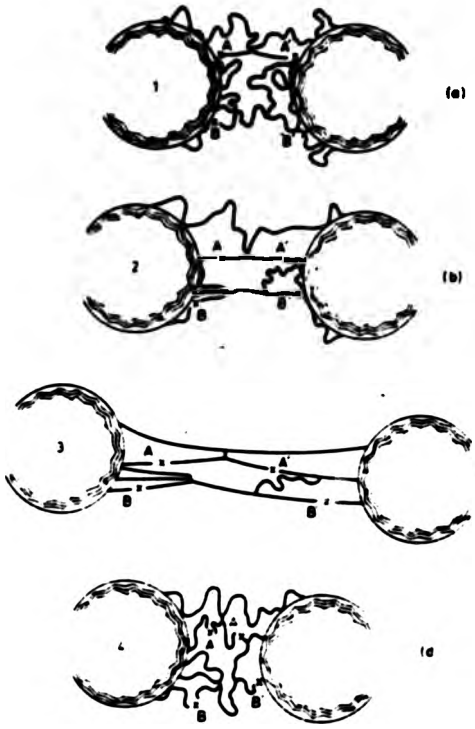


Fig. 2.15 Illustrating mechanism of reinforcement by molecular slippage. (a) original state; (b) intermediate elongation-shortest chain slipped beyond A and A'; (c) all chains fully stretched; (d) after retraction, all chains have equal lengths between particles.

initial cycle is viscous in nature, and the slippage process is accompanied by energy dissipation. This mechanism also indicates that high modulus is due to the sites of high (adsorptive) energy, and high strength is mainly due to the dissipation of energy by molecular slippage.

However, it should be noted that the investigators who formulated this hypothesis did not take account of possible effects which might arise from the presence of strong crosslinks in the rubber phase. Such crosslinks might impose some restriction on molecule slippage.

2.1.4 Rigidity of filler particle

Rigidity (as indicated by Young's modulus) is one of the properties of polymeric fillers which has been found to influence the reinforcement of rubbers. Various extensive studies have been carried out on this subject (5,8,9,55).

In 1938, Bacon *et al.* (5) carried out some experiments on the incorporation of polymethylmethacrylate and polyacrylonitrile synthetic latices in natural rubber latex. The synthetic latices were mixed with the rubber latex in a wide range of proportions and vulcanised with sulphur-butyl zimate dispersion. From the resultant vulcanised latices, films were prepared in the usual way by allowing the thin films to evaporate at room temperature. They found that polyacrylonitrile imparted a greater stiffening effect to the vulcanisate than did polymethylmethacrylate. Other studies carried out by Bacon and Schidrowitz (55) showed that polyacrylonitrile has a greater stiffening effect than polystyrene. Although Bacon and his co-workers did not take account of other parameters of the polymeric fillers and of possible chemical interaction between the filler particles and the natural rubber in which they were embedded, which might well influence the reinforcement of the vulcanisates, their observations have been confirmed by other workers

(8,9).

Morton et al. (8,9) carried out various studies of the effect of the modulus of polymeric fillers upon the tensile strength of filled vulcanisates. The studies involved two different systems : (I) the use of model polymeric fillers, such as polymethylmethacrylate, polystyrene, poly-2,6-dichlorostyrene and polyacenaphthylene; (II) thermoplastic elastomers prepared from styrene-diene-styrene triblock polymers. The polymeric filler particles were prepared as latices by emulsion polymerisation. They were then latex blended with styrene-butadiene rubber latex, compounded, coagulated, and vulcanised sheets prepared from the coagulum. The properties of the SBR vulcanisates containing the various fillers are shown in Figure 2.16. It is evident that the tensile strength of the filled vulcanisates depended upon the magnitude of the filler modulus. Figure 2.17 shows the effect of the variation in block length and styrene content on the stress-strain behaviour of styrene-butadiene-styrene (SBS) polymers. The stress levels increase with increasing styrene ("filler") content but are independent of the block lengths. Thus the centre block size does not exert the same influence as the "molecular weight crosslink" in a conventional vulcanisate. The tensile strengths of the materials to which Figure 2.17 refers are shown as the last points in the curves. These also increase with increasing styrene content, and this Morton et al. suggested could also be explained as a "filler" effect.

Morton et al. have proposed that in the case of the SBS block copolymers, strength reinforcement occurs because of the ability of the glassy domains to yield and absorb energy, thus delaying the onset of crack propagation. Energy dissipation is assisted by the efficient transmission of the applied stress through the elastic chains to the polystyrene domains as well as by the presence of some phase mixing at the interface between the polystyrene domains and the rubber phase. In this way,

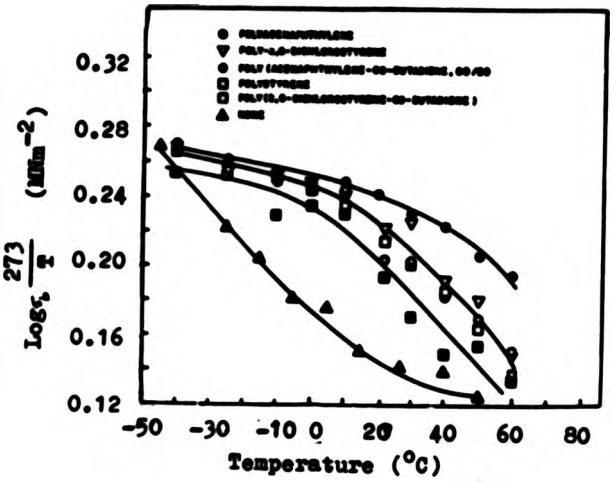


Fig. 2.16 Effect of various fillers upon tensile strength of SBR vulcanisates at various temperatures (8)

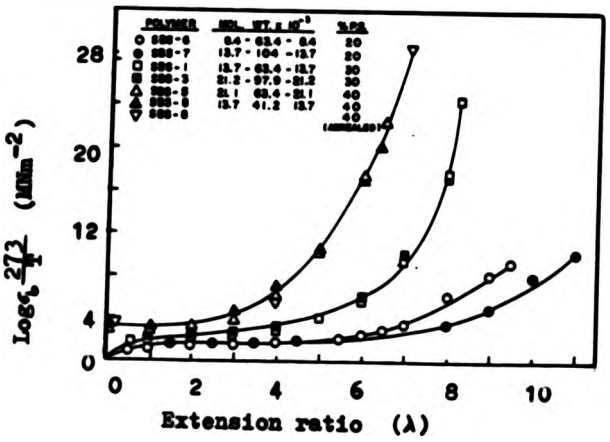


Fig. 2.17 Stress- strain properties of SBS elastomers (8)

the strength reinforcement increases as the dissipation of energy within the domains increases, e.g., as the glass-transition temperature of the domains is increased.

Payne (56) has provided evidence to support the hypothesis that a hard filler in a soft matrix creates a hydrodynamic disturbance which is accompanied by lengthening of the relaxation-time spectrum of the composite material. The presence of carbon black in filled vulcanisates will extend the time spectrum at long times and at high temperature by many decades. This is in almost complete agreement with the findings of Morton et al..

2.1.5 Distribution and dispersion of filler particles

Full reinforcement of a rubber by a particulate filler cannot be achieved unless the filler particles have been properly dispersed. Microscopic examination of filled vulcanisates has enabled the infuence of the quality of dispersion upon reinforcement to be studied. Various techniques (57-59) have been developed for the microscopic examination of rubber compounds. Light microscopy has been particularly useful. However, except in the case of coarse fillers, with little or no reinforcing ability, individual particles are not observed, but aggregates, in the form of either dispersed filler or flocculates, which consist of dense clusters of particles in close association with the rubber matrix are readily seen, though their actual structure can be revealed only by the electron microscope. All the types of microscopic examination of filled elastomer have shown that reinforcement increases with increasing quality of dispersion.

2.1.5.1 Effect of quality of carbon black dispersion

Various studies (60-62) have been carried out on the dispersion of carbon black in rubber in order to determine the extent to which changes in the degree of dispersion

correlate with extent of reinforcement. The minimum degree of dispersion which is necessary for the development of significant reinforcement has also been investigated. These studies have shown that tensile strength increases with increasing quality of dispersion, and that only very short mixing times are required for the development of good mechanical properties (60,61).

The effect of the quality of carbon black dispersion upon the tensile strength and tread wear resistance of oil-extended styrene-butadiene rubber vulcanisates is shown in Figure 2.18 (62). It can be seen that tensile

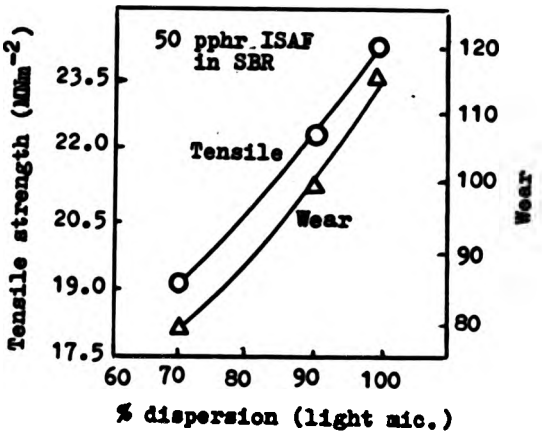


Fig. 2.18 Effect of the quality of carbon black dispersion upon tensile strength and wear resistance of styrene-butadiene rubber vulcanisates (62)

strength increased with increasing quality of dispersion. The quality of dispersion was quantified as the percentage of black which was dispersed as aggregates below 9000 nm in size. These percentages were obtained by the Leigh-Dugmore method (63). Microtome sections were measured for total area covered by the black agglomerates down to 9000 nm in size. This was done under a light microscope with a

finely-calibrated net micrometer eyepiece. The percentage of carbon black in the form of aggregates not less than 9000 nm in size for each stock was then calculated as the ratio of this measured area to the total area on the section represented by black. This latter value is a function of both the black loading and density of the components.

2.1.5.2 Effect of quality of polymeric filler dispersion

Various reinforcement studies of latex films by polymeric fillers which have been carried out by various workers, notably, by Morton *et al.* (6-9) have shown that uniform dispersion of the individual filler particles in the rubber matrix is aprerequisite for effective reinforcement. Replica electron microphotographs were taken of the fracture surface of the elastomer-filler mixtures and vulcanisates in most cases, in order to observe the state of dispersion. However, these authors have not published results in graphical form which demonstrate the effect of quality of polymeric filler dispersion upon mechanical properties of filled polymers.

2.2 Theories of reinforcement

The mechanism of reinforcement which leads to changes in the viscoelastic response of filled elastomers is far from clear. Much less has a satisfactory theoretical treatment of the phenomenon been developed. This is not surprising because the factors which influence reinforcement are inter-related, and, as such, it is not easy to develop mathematical equations which take all the factors into account.

2.2.1 Hydrodynamic effect

Several attempts have been made to derive equations for the modulus of an elastomer which contains dispersed

particles. The earliest of these attempts was by Smallwood (64), who proposed an equation analogous to the equation (65) for the viscosity of dilute dispersions of spherical particles in a liquid, namely,

$$E = E_1(1 + 2.5C_2) \qquad 2.1$$

where E and E_1 are the modulus of the filled and unfilled vulcanisates respectively. C_2 is the filler volume fraction, the factor 2.5 is the Einstein coefficient.

Unfortunately, this equation holds for low concentration of filler only and various amendments have been proposed (16,66,67). Thus, Guth and Gold (67) considered the interactions between pairs of particles, and added a term involving the square of the concentration of filler, thereby obtaining

$$E = E_1(1 + 2.5C_2 + 14.1C_2^2) \qquad 2.2$$

For non-spherical particles Guth (68) introduced a shape factor *f*, defined as the ratio of the diameter to the width of a particle, and proposed

$$E = E_1(1 + 0.67fC_2 + 1.6f^2C_2^2 + \text{----}) \qquad 2.3$$

These equations were derived on the assumption that the medium wets the filler particles, but does not chemically react with the filler surface.

A number of empirical equation have been proposed to describe the reinforcing effect of spherical filler particles. An empirical equation suggested by Eilers and Dijck (69) is

$$E = E_1\left[1 + \frac{1.25C_2}{1 - 1.28C_2}\right] \qquad 2.4$$

Brinman (70) proposed the equation

$$E = E_1(1 - C_2)^{-5/2} \qquad 2.4a$$

One of the most elaborate empirical equations that have been proposed to describe the reinforcing effect of spherical filler particles is that due to Kerner (71), whose complete equation is

$$G = G_1 \left[\frac{\dfrac{C_2 G_2}{(7 - 5V_1)G_1 + (8 - 10V_1)G_2} + \dfrac{C_1}{15(1-V_1)}}{\dfrac{C_2 G_1}{(7 - 5V_1)G_1 + (8 - 10V_1)G_2} + \dfrac{C_1}{15(1 - V_1)}} \right] \qquad 2.5$$

where G is the shear modulus, V is the Poisson's ratio of the matrix, and C is the volume fraction of particles. The subscripts 1 and 2 refer to the matrix and filler respectively.

Lewis (72) and Nielsen (73) have shown that the Kerner equation can be put in a more general form

$$\frac{M}{M_1} = \frac{1 + ABC_2}{1 - B\psi C_2} \qquad 2.6$$

where M represents any particular modulus, i.e., shear, Young's modulus or bulk. A is a constant which take into account such factors as the geometry of the filler phase and the Poisson's ratio of the matrix. The quantity A is related to the generalised Einstein coefficient, k_E

$$A = k_E - 1 \qquad 2.7$$

$$k_E = 2.5/\psi_m \qquad 2.7a$$

where ψ_m is the volume fraction of an agglomerate that is made of spheres. B is a constant which takes into account the relative modulus of the filler and matrix phases (M_2/M_1) its value is 1.0 for any large M_2/M_1 ratio. The quantity B is defined as

$$B = \frac{M_2/M_1 - 1}{M_2/M_1 + A} \qquad 2.8$$

Ψ is an empirical function which depends upon the maximum packing fraction C_m of the filler. An empirical function which satisfies the necessary boundary condition is

$$\Psi = 1 + \left[\frac{1 - C_m}{C_m^2}\right]C_2 \qquad 2.9$$

As has been pointed out above, the effects of particulate fillers upon all the elastic moduli can be predicted by the use of the modified Kerner equation. For instance, for composites filled with particles which are nearly spherical shape, the shear modulus, according to the modified Kerner equation is given by :

$$\frac{G}{G_1} = \frac{1 + ABC_2}{1 - B\Psi C_2} \qquad 2.10$$

where the value of A for any matrix Poisson's ratio in this case is

$$A = \frac{7 - 5V_1}{8 - 10V_1} \qquad 2.11$$

and

$$B = \frac{G_2/G_1 - 1}{G_2/G_1 + A} \qquad 2.12$$

A few problems have been encountered in attempting to confirm the applicabilty of the above theoretical expression. Firstly, none of the equations contains the size of the filler particles. However, experiments generally show an increase in modulus (or viscosity in the case of suspensions) as the particle size decreases (6-9,13,14,72). Secondly, the equations assume that there is good adhesion between the filler and the matrix. In view of the limited applicability of these equations, various

theories have been put forward which take into account various filler characteristics and interaction between the surface of the filler particles and the rubber matrix.

2.2.2 Polymer-filler adhesion effect

Several attempts (3,23-25,74,75) have been made to assess the contribution towards reinforcement made by adhesion between the filler and the matrix. Rehner (3) has put forward an equation which quantifies the way in which rubber-filler attachments may cause reinforcement by making use of classical elasticity theory. Blanchard and Parkinson (23) have also postulated a semi-empirical relationship base on the concept of filler attachment and on the kinetic theory of rubber elasticity. Their equation is

$$F = 1.62G(1 - \alpha^{3})\exp\{0.31(\alpha - 1)\} + \mu(\alpha - 1)^{4} \qquad 2.13$$

where F is the force per unit area of original cross section, α is the extension ratio (i.e., the ratio of the extended length to the initial length). G is the shear modulus, μ is an empirical constant. Since $\mu \rightarrow 0$ for gumstocks, G is proportional to kT as in the kinetic theory of rubber elasticity

$$F = \nu kT(\alpha - \alpha^{2}) \qquad 2.14$$

where ν is the number of effective network chains per unit volume and kT is the product of the Boltzmann constant and the absolute temperature. Thus G in equation (2.13) is proportional to the concentration of effective network chains.

Blanchard and Parkinson attribute qualitative significance to the two empirical parameters, G and μ. They considered G to be a measure of the number of crosslink points within the rubber. The significance of μ was not clearly established. They believed μ to represent some measure of the network chains between the particles.

These network chains cannot exceed their limit of extensibility without breaking. The authors partitioned G into the sum of two parts as follows :

$$G = G^* + G_r F(x) \qquad 2.14$$

where G^* represents the effect of strong linkages within the network. G_r is a constant which is proportional to the total number of linkages which can easily be broken by pre-stressing. Blanchard and Parkinson speculated that these linkages might represent the effect of Van der Waals forces and the associated adsorption phenomenon at the filler surface. The function F(x) was defined as the fraction of G_r which still remain after all the weak bonds with strength less than x have been broken. The authors attributed the softening effect to breakage of the weak linkages represented by G_r. The value G^* was considered to be constant, since it represents the modulus effect of the very strong linkages.

Pursuing this hypothesis of Blanchard and Parkinson, Bueche (24,25) has approached the problem of stress softening in a somewhat different manner. Although the theory of Bueche explains the Mullins effect (stress softening) reasonably well, it involves the assumption that attachments to filler particles move affinely during the deformation. This assumption is not realistic in filled vulcanisates, because the internal deformation is not the same as the "apparent" or external deformation in the case of heterogeneous systems. Therefore, when a filled rubber system is subjected to an applied force, the displacement of interior points (or of filler particles within the material) would be different from that predicted from appartent deformation assuming that deformation occurs affinely.

There exist other theories (74,75) which take into account the dependence of adhesion between polymer and filler on the magnititude of the applied stress, as the stress often determines whether or not there is good

adhesion. Nielsen et al. (74) have proposed the following empirical equation

$$G = G_1C_1 + QG_2C_2 \qquad 2.16$$

where C is volume fraction of filler, G is shear modulus, and the subscripts 1 and 2 refer to the matrix and the filler respectively. Q is a factor which characterises the adhesion between the two phases. Q varies from zero to one; the lower the value, the poorer is the adhesion. Although this equation allows for the effect of rubber-filler adhesion, it does not make allowance for either particle size or shape.

Sato and Furukawa (75) have put forward a more detailed theory based upon the concept of internal deformation. The authors have attempted to make quantitative allowance for the contribution towards reinforcement made by adhesion between filler and matrix. Their equation is as follows :

$$E = E_1\left[\left[1+\frac{y^2}{2(1-y)}\right](1-\Psi\tau)+ K\frac{y^3(1-y/2)}{(1-y)^2}(1-\Psi\tau)-\frac{y^2}{(1-y)}K\frac{\Psi\tau}{y^3}\right] \qquad 2.17$$

[volume effect] [surface effect] [cavitation effect]

where y is $C_2^{1/3}$, C_2 being the volume fraction of the dispersed unit, K is the amplifying factor, defined as

$g_f/g_r = g_f^{(m)}(1 - \tau)/g_r^d$

$g^{(m)}$ is the number of chains per unit area in the ideal case

g_f is the number of chains per unit area in the actual specimen

g_r is the number of chains per unit volume

d is the diameter of dispersed unit

τ is the adhesion factor, and

$\Psi = y^3(1 + y - y^3)/3(1 - y + y^2)$

When the bond or adhesion between filler and matrix is weak, the bond may break on application of load. In such a case, the rubber matrix will deform more than the filler, so that elliptical cavities or voids develop around each filler particle. The term which accounts for surface effects, as indicated in equation 2.17, would vanish, and one would expect a lower modulus. But if there exists a strong adhesion between the two phases, increased modulus would be expected.

2.2.3 Particle size effect

The various theories of reinforcement considered so far have not made full allowance for the size of the filler particle. For example, Guth's equation (2.3) includes a shape factor but not a size factor. A more detailed molecular theory (Equation 2.17) of filler reinforcement which takes into account other effects, such as volume, surface and cavitation, makes some allowance for particle size, but only indirectly. However, Alter (13) has published results in graphical form which demonstrate the effect of filler particle size upon the mechanical properties of filled polymers. Alter has described the family of curves shown in Figure 2.5 (Section 2.1.2.1) by the equation

$$E/E_1 = 1 + g(v)/d + \text{-----} \qquad 2.18$$

where d is the particle diameter and g(v) is the variation of the slope of the relationship between E/E_1 and $1/d$ with volume concentration. The above equation (2.18) is somewhat similar to the equation of Guth (2.3). Alter has found that a plot of the slope of each of the lines in Figure 2.5 against v is linear. The function g(v) is approximately

$$g(v) = 0.03 + 0.8v \qquad 2.19$$

Plots of the original data for polyethylene as E/E_1 versus v have been found to be linear up to about $v = 0.2$. However, the data did not fit Guth's equation.

Alter put forward two possible hypotheses to explain the 1/d dependency. The first is that 1/d is a particle shape factor correction, as proposed by Guth. The second is that the 1/d function expresses a dependence on the surface-to-volume ratio of the filler particles.

2.2.4 Filler agglomeration effect

Many of the theories discussed above assume complete dispersion of the individual particles. In normal practice, this does not occur. There is a tendency for many particles to form agglomerates both before compounding and when incorporated in the polymer matrix (Section 2.1.5). The occurrence of these agglomerates gives rise to local heterogenity of mechanical properties especially where air pockets trapped within the agglomerates can lead to premature fracture of the composite. There appears to be very little published work concerning either the theoretical or graphical description of the effects of filler agglomerates upon the reinforcement of rubbers. Guth (76) has made an attempt in this direction, having derived an expression for the modulus of a carbon black-filled elastomer which takes into consideration the tendency of carbon black particles to agglomerate into chain-like clusters.

Mooney (77) has proposed an expression for the viscosity of a suspension of spheres in a liquid by modifying the Einstein equation (65). The equation of Mooney can be expressed in the form

$$\ln\frac{\eta}{\eta_l} = \frac{2.5C_2}{1 - SC_2} \qquad 2.20$$

where η is the viscosity of the system containing the

filler, η_1 is the viscosity of the pure liquid, C_2 is the volume fraction of the filler, and S is the "crowding factor" or "relative sedimentation volume" of the filler. S is defined by the equation

$$S = \frac{\text{apparent volume occupied by the filler}}{\text{true volume of the filler}} \qquad 2.21$$

The minimum value that S can have is 1.0. For close-packed spheres of uniform size, S = 1.32. Experimental values of S range from about 1.2 to over 2.0. When Mooney used a value of S = 1.43 to describe the experimental data of Vand (78) for the relative viscosity of a suspension of glass spheres in zinc iodide solution of viscosity 69.8 $mNsm^{-2}$, the agreement between theory and experiment up to volume fractions of over 0.50 was good. A value of S = 1.4 was also found to fit the best experimental values of viscosity analysed by Rutgers (79) up to volume fractions of over 0.50. To the extent that equations for the viscosities of lyophobic sols can also be used to represent the variation of the elastic modulus of filled rubbers with concentration of filler particles, the equation of Mooney can be used to calculate the shear modulus of the systems filled with spherical particles. At concentrations below volume fractions of filler of 0.2, the Mooney equation agrees with the Guth equation.

2.3 Behaviour of polymeric filler particles in films which are obtained directly from natural rubber latex

One of the virtues of natural rubber latex for the production of dipped goods is that it gives films of which, when vulcanised, have high tensile strength and extensibility. This enables it to be used in a wide variety of applications subjected to stress without any need for reinforcement. However, thin walled articles,

such as household gloves may fail in service because of tearing or puncturing, and there may be occassions when the tear resistance shown by films from natural rubber latex as normally compounded is considered inadequate. Gorton (80) has shown this to be the case while investigating the causes of failure of household gloves in service.

The behaviour of various polymeric fillers in post-vulcanised natural rubber latex films has been investigated by Gorton (80). One of the fillers discussed by Gorton is Heveaplus MG polymer, which is prepared by graft polymerisation of methylmethacrylate monomer in natural rubber latex. Structurally, the MG polymer appears to consist of a cis-polyisoprene "backbone" which has a small number of relative long side chains of polymethylmethacrylate. Although MG polymer latices can be prepared at almost any desirable ratio of polymethylmethacrylate to rubber, the most commonly-used polymers contain 30 and 49 per cent of polymethylmethacrylate. These polymers are designated as MG30 and MG49 respectively. Gorton found that adding 0-30 parts of the various MG polymer particles increased the tensile strength, tear strength and puncture strength of a glove vulcanisate as given in Table 2.2. Alteration of the vulcanisation system or addition of antiozonant and antioxidant to the latex did not give improved mechanical properties as compared with the addition of the MG polymer particles, which substantially enhanced the mechanical properties of the latex films. It can be seen in Table 2.2 that the films from the latex containing MG15 polymer particles show some improvement in tensile strength, tear strength and puncture strength. The elongation at break was hardly altered, but the modulus showed some increase, e.g., at 30 pphr of MG15 polymer particles, the 100% relaxed modulus increased by 38%. The tear strength and the punture strength become higher as the level of MG15 polymer particles increased. The effect of MG30 polymer particles upon the properties of latex films followed a

Table 2.2 Properties of NR latex films containing MG polymers (80)

Additive	Tensile strength MNm^{-2}	Elongation at break %	300% modulus MNm^{-2}	Tear strength N	Puncture strength N
pphr					
None	28.8	903	1.27	15.3	6.4
5-MG15	38.9	898	1.84	20.7	8.8
10-MG15	37.7	896	1.74	16.6	9.8
20-MG15	37.5	891	1.73	18.2	11.4
30-MG15	38.5	876	1.85	24.2	11.5
5-MG30	39.8	908	1.61	22.5	9.5
10-MG30	37.2	854	1.95	43.5	11.9
20-MG30	36.5	842	2.20	30.0	19.5
30-MG30	33.5	811	2.54	35.4	20.5
5-MG49	34.9	860	1.89	21.2	8.9
10-MG49	33.3	820	2.25	20.4	9.4
20-MG49	29.1	760	3.21	52.2	14.6
30-MG49	25.6	685	4.34	45.3	12.7

Table 2.3 Properties of NR latex films containing various fillers (80)

Additive	Tensile strength MNm^{-2}	Elongation at break %	300% modulus MNm^{-2}	Tear strength N	Puncture strength N
pphr					
10-Vinamul 3400	29.2	892	1.38	15.0	8.9
20-Vinamul 3400	27.1	890	1.48	18.7	9.9
30-Vinamul 3400	23.9	863	1.56	54.3	11.1
10-Vinamul 6825	25.1	895	1.21	14.6	9.8
20-Vinamul 6825	25.2	903	1.20	23.4	10.9
30-Vinamul 6825	23.7	905	1.31	32.9	10.1
10-Vinamul 7700	27.5	837	1.58	16.9	8.4
20-Vinamul 7700	22.1	750	2.03	30.3	7.8
30-Vinamul 7700	20.2	710	2.59	17.9	9.6

Table 2.4 Properties of NR latex films containing carboxylated polymers (80)

Additive	Tensile strength MNm^{-2}	Elongation at break %	300% modulus MNm^{-2}	Tear strength N	Puncture strength N
pphr					
None	28.8	903	1.27	15.3	6.4
10-Breon 9370	24.6	973	1.06	18.4	10.2
20-Breon 9370	21.9	956	1.09	16.0	10.8
30-Breon 9370	15.6	911	1.17	13.6	10.1
10-Breon 1577	24.8	828	1.40	24.6	9.6
20-Breon 1577	21.3	799	2.04	40.9	6.9
30-Breon 1577	16.7	736	2.00	43.9	12.4
10-Perbunan 310C	31.6	842	1.95	29.9	9.2
20-Perbunan 310C	25.2	775	2.27	32.9	10.9
30-Perbunan 310C	21.6	716	3.00	30.0	11.9
10-Perbunan 4R128	30.8	888	1.33	25.7	8.6
20-Perbunan 4R128	29.5	904	1.26	26.8	7.6
30-Perbunan 4R128	28.6	915	1.09	29.5	11.7
10-Perbunan SN15M	32.2	916	1.28	27.1	7.6
20-Perbunan SN15M	29.2	855	2.73	70.0	11.0
30-Perbunan SN15M	21.6	809	2.91	50.0	10.7

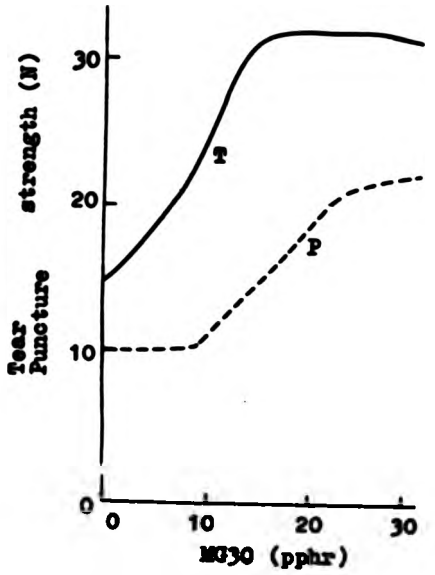


Fig. 2.19 Effect of MG30 upon the tear strength (T) and puncture strength (P) of NR vulcanisates (80)

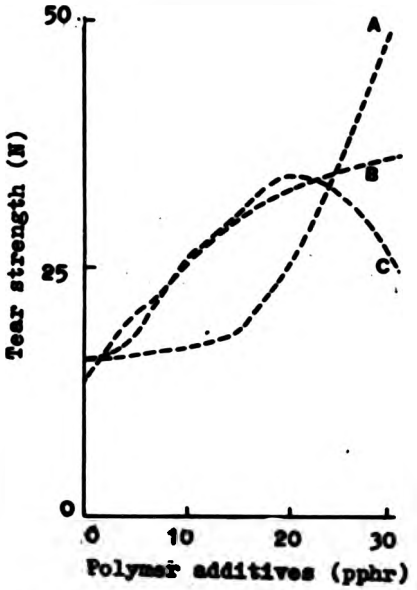


Fig. 2.20 Effect of 3400(A), 6825(B) and 7700(C) upon the tear strength of NR vulcanisates (80)

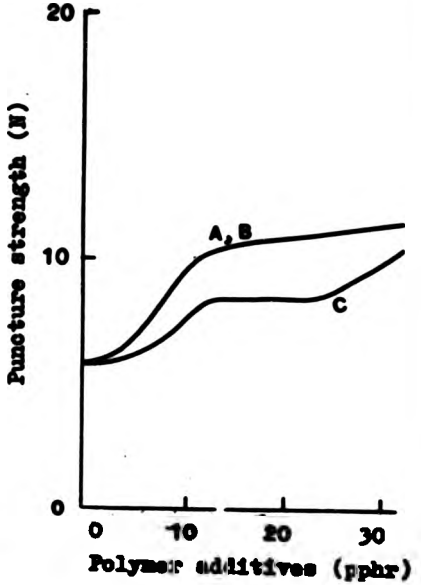


Fig. 2.21 Effect of 3400(A), 6825(B) and 7700(C) upon the puncture strength of NR vulcanisates (80)

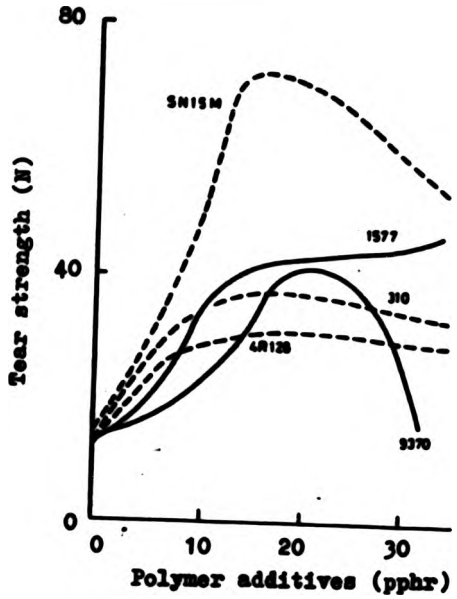


Fig. 2.22 Effect of 1577, 9370, 310, 4R128 and SN15M upon the tear strength of NR vulcanisates (80)

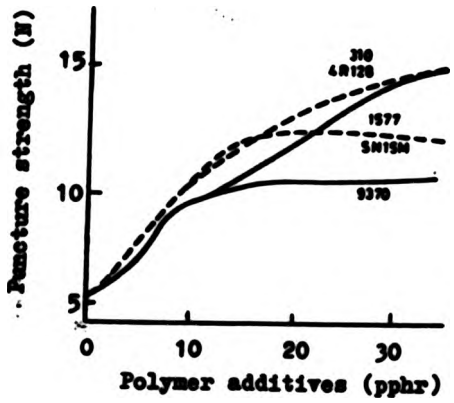


Fig. 2.23 Effect of 1577, 9370, 310, 4R128 and SN15M upon the puncture strength of NR vulcanisates (80)

similar pattern, except that the overall tear strength and puncture strength values were higher than with MG15 polymer particles. The influence of MG30 polymer particles upon tear strength and puncture strength of the film vulcanisates is shown in Figure 2.19.

In the same paper, Gorton has reported essentially similar results for the following polymeric filler particles :

I) vinyl acetate/vinyl chloride/ethylene terpolymer particles (Vinamul 3400),
II) vinyl acetate/ethylene copolymer particles (Vinamul 6825),
III) polystyrene particles (Vinamul 7700),
IV) carboxylated acrylonitrile-butadiene copolymer particles (Breon 9370 and 1577, and SN15M),
V) carboxylated styrene-butadiene copolymer particles (Perbunan 310C),
VI) carboxylated polychloroprene particles (Perbunan 4R128).

The effects of these particles upon the mechanical properties of films obtained directly from natural rubber latex are given in Tables 2.3 and 2.4, and shown in Figures 2.20 - 2.23. Gorton concluded by saying that a number of polymeric filler latices when blended with natural rubber latex reinforce the latex compound by enhancing resistance to tearing and puncturing without greatly affecting the other strength properties. Strictly speaking this not true. Of the various fillers examined in his investigation, Gorton was of the opinion that the MG polymer particles were the most effective in reinforcing latex films.

The effects of polymeric filler, such as polyvinyl-chloride particles, upon the mechanical properties of films from natural rubber latex have also been investigated by King (81). The types of polyvinylchloride that have been used include Breon 351, Breon 576, Breon

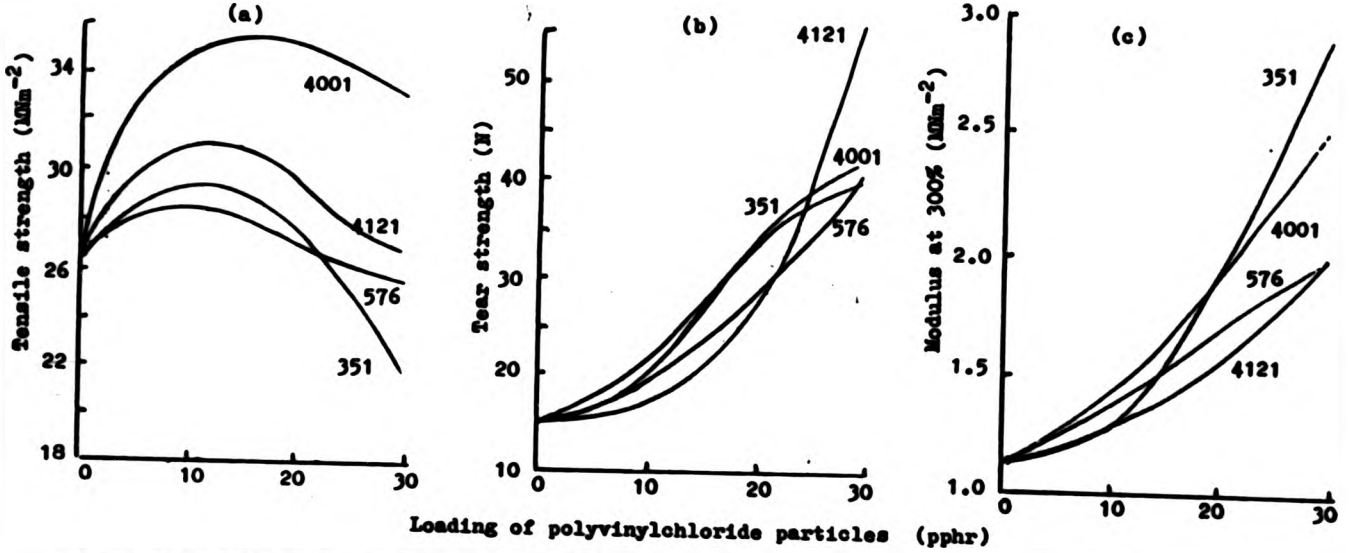


Fig. 2.24 Effect of polyvinylchloride filler particles upon the mechanical properties of films derived from NR latex. Films were cured at 100°C for 30 minutes. Figures appended to curves indicate type of polyvinylchloride (81)

4001 and Breon 4121. The tensile strength, modulus at 300%, elongation at break, tear strength and hardness of the film vulcanisates were determined. The puncture strengths of the film vulcanisates were not determined. In his discussion, King argues that the tensile strength of the film was enhanced at low filler loading passing through a peak at 10-20 pphr loadings, with films containing Breon 4001 giving optimum values. He also reported that hardness and modulus at 300% increased, and that there was some reduction in elongation at break. As regards tear strength, King reported that all the various polyvinylchloride particles investigated enhanced the tear strength of the film vulcanisates. However, he had some difficulty explaining this behaviour. Electron micrographs of the fractured surface of the films from the blends of natural rubber and polyvinylchloride latices give the appearance of a homogeneous mass. The homopolymers appear to be present as discrete particles. The effects of these particles upon the tear strength, tensile strength and modulus at 300% extension of films derived from natural rubber latex as reported by King (81) are shown in Figure 2.24.

The possibility of reinforcing film obtained from prevulcanised natural rubber latex by added polymer particles has also been investigated (82). As already discussed above, films derived from unvulcanised natural rubber latex can be reinforced by a number of polymeric fillers. However, many manufacturers of dipped articles use prevulcanised rubber latex rather than the vulcanisable unvulcanised rubber latex which was used in the work reported by Gorton and others. Some workers from London Rubber Company (82) have attempted to use the polymeric fillers referred to in the Gorton paper and others, with prevulcanised natural rubber latex. They found that none of the polymeric fillers referred to in the Gorton paper gave any increase in the tear strength and puncture strength of films obtained from prevulcanised natural rubber latex. However, they were surprised to find

Table 2.5 Effect of polyvinylchloride particles upon the mechanical properties of films from NR latex (81)

PVC loading pphr	Tensile strength MNm^{-2}	Elongation at break %	Modulus at 300% MNm^{-2}	Tear strength *	Puncture strength *
None	29.8	789	1.95	0.052	21.6
2.5	26.6	819	1.75	0.084	18.3
5.0	29.1	784	2.01	0.075	20.9
7.5	28.6	811	2.12	0.107	24.8
10.0	27.4	784	2.33	0.102	23.8
12.5	25.6	770	2.23	0.081	21.0
15.0	22.0	680	2.97	0.083	18.7
20.0	22.6	623	3.48	0.071	19.7

* Units not given

that films from prevulcanised natural rubber latex containing 5 to 10 pphr, preferably about 7.5 pphr, of polyvinylchloride particles showed significant improvement in tear strength and punture strength without any deleterious effect on other strength properties. These results are given in Table 2.5. However, no reason was given by these workers as to why polymeric fillers reported as giving improvements in the tear strength and puncture strength of films obtained from vulcanisable unvulcanised natural rubber latex behave differently in films obtained from prevulcanised natural rubber latex.

It is evident from these studies that films obtained directly from rubber latices can be reinforced by polymeric filler particles. However, as previously stated, these studies have been empirical in nature and little has emerged concerning the principles which underlie the reinforcement of rubber films produced in this way. A detailed investigation of these principles is therefore appropriate in the present work.

2.4 Formation of films from polymer latices

The preparation of dry films from rubber latices and from blends of rubber latices and polymeric filler latices during the course of this work often presented problems. In some cases, it was extremely difficult to obtain latex films from blends which contained high concentration (> 20 pphr) of polymeric filler, due to film cracking. Thus it was necessary to consider the mechanism of the formation of dry films from latices. A brief survey of some of the literature on this subject and of the related subject of the structure of films obtained from latices is presented below.

2.4.1 Mechanism of formation of dry films from polymer latices

Film formation from polymer latices is a much more

complicated process than film formation from polymer solutions. This is because both the initial latex and the final film are heterogeneous (83). Polymer latices comprise colloidal dispersions of submicroscopic polymer particles in a dispersion medium which is usually water. Latices have dual character. They are colloidal because the latex is a colloidal sol, and they contain polymeric material, each colloidal particle having the same properties as the bulk polymer. Some latices are able to form tough transparent continuous films on drying, whilst others form friable, opaque, discontinuous films, according to the composition of the polymer and the conditions of drying.

Dillion et al. (84) were the first to propose a mechanism for film formation from latices. They postulated that the latex particles coalesce by viscous flow, with the great change in interfacial area between polymer and dispersion medium providing the driving force.

Brown (85) postulated that capillary forces rather than the surface tension forces proposed by Dillion et al. were the main source of energy for the film-formation process. Brown showed that the forces arising from double layer repulsion and London-Van der Waals attraction were not significant, and that film formation occured when the capillary force was greater than the force which resisted deformation. Brown also pointed out that : (I) film formation occurs concurrently with the evaporation of water; (II) the rate of water removal may determine the coalescence of borderline film-forming latices; (III) porous, incompletely coalesced films may be formed by maintaining the temperature below a critical value; and (IV) there is a maximum viscosity for film formation for each polymer type.

Voyustkii (86) argued that the surface tension forces postulated by Dillion et al. (84) and capillary forces postulated by Brown (85) could not account for the mechanical properties exhibited by latex films. He suggested the occurrence of "autohesion", i.e., the mutual

interdiffusion of free polymer chain ends across the particle-particle interface in the coalesced film, which makes the latex film homogeneous and thus improves its mechanical properties.

Many workers have speculated on the fate of the emulsifier and the other non-polymeric ingredients of the latex during film formation. For example, Wagner and Fischer (87) stated that the latex films are not homogeneous, but rather consist of two interpenetrating networks of polymer and emulsifier. Voyustkii and Starkh (88) stated that the emulsifier could remain in the film as an independent network or it could dissolve in the polymer.

Vanderhoff (89) attempted to reconcile the theories of Dillion et al. (84) and Brown (85) by showing that the surface tension and capillary forces are complementary. He also provided some experimental evidence for the occurrence of autohesion, and the fate of the emulsifier. Vanderhoff proposed the following mechanism for the formation of dry films from latices. Initially, the latex particles move about freely, with Brownian motion. As the water evaporates, their motion becomes more restricted and eventually the water-air interfacial tension forces them together in a packed array, with their double layers hindering their mutual approach. The continued evaporation of the water exerts a force to overcome this repulsion so that the double layers are "ruptured" and a polymer-polymer contact is formed. This brings the polymer-water interfacial tension into play, to reinforce and complement the water-air interfacial tension. If the combined forces are sufficient to deform the polymer spheres, they form a continuous film. Vanderhoff argued that the film becomes more homogeneous upon ageing because there occurs a further gradual coalescence (the rate of which depends upon the polymer) during which any incompatible substance is exuded to the surface.

The effect of experimental variable upon the formation of dry films from latices has been studied by

electron microscopy (90), and the theories of film formation, including the role of autohesion, have been reviewed (91).

2.4.2 Structure of dried films from rubber latices

2.4.2.1 Post-vulcanised latex films

In post-vulcanised films, the non-rubber substances present in natural rubber latex exert both chemical and physical effects. The latex comprises discrete rubber particles which are enclosed in a surface-active interfacial film consisting mainly of proteins, soaps and phospholipids. The particulate structure in post-vulcanised films can be visualised by soaking the film in water. Because the refractive index of the protein remaining between the particles is altered, the rubber and protein become distinguishable under the microscope (92).

Chong and Porter (93) carried out an investigation to determine the structure of latex vulcanisates by determining the concentrations of physically-effective crosslinks. The method was originated by Mullins (94). Also, the proportion of sulphur combined with the rubber in forms other than crosslinks was determined by a method originally devised by Saville (95). Chong and Porter obtained evidence which pointed strongly to the persistence of "structure" in vulcanised cast films from natural rubber latex. They also confirmed the involvement of proteins in the structure. They found that, during the formation of a continuous film by evaporation of natural rubber latex, the protein which initially surrounds each rubber particle and stabilised it in the latex, appears to form rather hard domains which behave like particulate fillers (Fig. 2.25), affecting the stress-strain behaviour and enhancing the modulus. Removing the protein enzymically or hydrolytically, or disrupting and dispersing the domains by mechanical working, cause the filler effects to disappear.

The chemical effects were mainly due to the process of nitrogeneous bases which increase the rate and efficiency of vulcanisation.

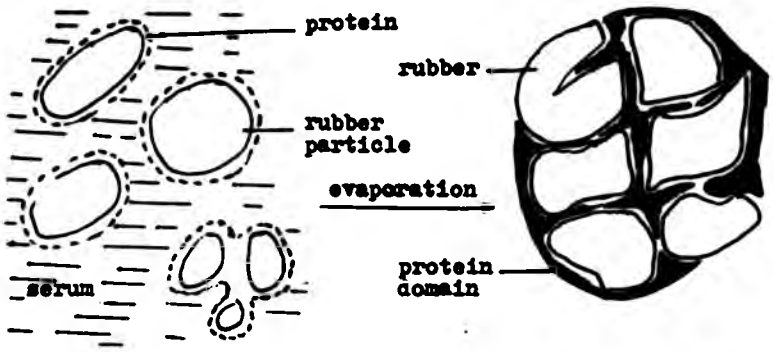


Fig. 2.25 Development of physical structure in a film obtained from high-ammonia natural rubber latex by evaporation (93)

2.4.2.2 Prevulcanised latex films

It is not intended in this thesis to enter the controversy concerning the structure of prevulcanised latex films. However, it is of considerable interest to have a knowledge of the nature of the forces which hold the individual particles of such a latex together to form a continuous film. Three theories have been proposed to explain the strength of films from prevulcanised latex (96).

In the first theory, the strength is attributed to primary valence bonds formed between molecules of adjacent particles. It is presumed that these inter-particle bonds are formed during the drying of the latex films because other evidence proves that the intra-particle bonds are formed during the prevulcanisation reaction. However, it is found that strong, coherent films are formed even when

films are produced under conditions which are most unlikely to cause the formation of crosslinks between particles, thus invalidating the theory.

The second theory regards the film as made up of discrete particles of vulcanised rubber cemented together by means of non-rubber constituents derived from the initial latex. Thus removal of the non-rubber constituents should cause the film to disintegrate. Humphreys and Wake (97) have carried out an experimental test of this hypothesis, and found that the removal of the non-rubber constituents has no effect upon the strength of the vulcanised latex films.

The third theory seeks to explain the strength of the films in terms of secondary valence bonds formed between the molecules of adjacent particles. Each particle contains a large number of individual rubber molecules which are arranged in a tangled, haphazard manner. During the vulcanisation reaction, all the molecules of any one particle become linked to one another so that the particle becomes one giant network. Although the secondary valence bonds set up between any two molecules of adjacent particle will be very weak, the totality of such forces between two given particles becomes appreciable as each particle contains a large number of segments of rubber molecules capable of interacting with similar segments on a neighbouring particle. This third theory is regarded as the most convincing since it explains, to some extent, the observed properties of prevulcanised latex films, such as tensile stress-strain behaviour and behaviour towards solvents (97).

CHAPTER THREE : SURVEY OF LITERATURE PERTAINING TO PREPARATION OF LATICES OF CORE-SHELL POLYMERS BY EMULSION POLYMERISATION

3.1 Introduction to emulsion polymerisation

Emulsion polymerisation is an important technological process for the prodution of polymers industrially. It has also been used in the laboratory to prepare model spherical rigid polymeric fillers such as polystyrene, polymethylmethacrylate, polyacenaphthylene and various vinyl copolymers and terpolymers. The polymerisation is carried out in a system which normally comprises four essential components namely monomer, a dispersion medium (usually aqueous) in which the monomer is but sparingly soluble, soaps or other micelle-forming substances, and a water – soluble initiator. The reaction system remains fluid for the full course of the reaction. Heat dissipation is no problem, and, provided that the reaction system has been appropriately formulated, there is usually very little tendency for the particles to coalesce as the reaction proceeds. Furthermore, the product is obtained as a latex, and this is an advantage if it is desired to use the polymer in latex form (as is the case in the present work).

Detailed consideration of the theory and practice of emulsion polymerisation has been given by Blackley (1). His book sets out the various theories of emulsion polymerisation, and discusses in detail matters such as initiation, stabilisation, monomers and other components such as sequesters and short stops.

Basically, there are three different ways in which emulsion polymerisation reactions can be carried out in practice : (I) by batch process in which all the ingredients are added to the polymerisation reactor, and the mixture is heated with stirring to the polymerisation temperature; (II) by semi-continuous or semi-batch process

in which neat or pre-emulsified monomer (and sometimes initiator and emulsifier) are added continuously or incrementally to the reaction mixture at the polymerisation temperature; (III) by continuous process, in which all the ingredients are added continuously to one part of the polymerisation system and partially or completely converted latex is removed continuously from another part. In the case of continuous processes, the polymerisation reactor may comprise a single continuous stirred tank reactor, a series or cascade of continuous stirred-tank reactors, a loop or tube reactor, or a combination of any of the foregoing reactors.

3.2 Processes for carrying out core-shell emulsion polymerisation

In the past two decades, numerous patents have been claimed on the polymerisation of particles with a "core" composition which differs from that of the "shell". Representative patents include those by Ferry *et al.* (2), Purvis and Grant (3), Goodman *et al.* (4) and Herman *et al.* (5). This topic has also attracted the attention of workers in the field of emulsion polymerisation as a means of producing either larger particles than can be achieved in a single-stage reaction (6) or controlled surface charge densities in "model" systems (7).

A variety of methods have been used for preparing core-shell polymer latices. These fall into three broad categories :

(a) 'Conventional' processes, where either (I) the comonomers are both charged at the start of the reaction or (II) one monomer is charged at the start of the reaction, and the second monomer fed in slowly throughout the course of the reaction;

(b) 'Seeded-growth' processes, where one monomer is first polymerised to form what is effectively a seed latex, and the second monomer is then added

to this "core" latex and polymerised;

(c) 'Shot-growth' processes, where a seed latex is only partially polymerised (usually to a conversion exceeding 60%) before the second monomer is added - such processes are in effect compromises between conventional and seeded-growth processes.

The most commonly adapted process used in industrial practice seems to be (a)(II), where surfactant is also progressively added. The feasibility of process (a)(II) depends very much upon such processes as the copolymerisation behaviour of the two monomers and the relative solubilities of the two monomers in the dispersion medium. Both seeded-growth and shot-growth processes have been extensively studied by various workers (e.g., 8 - 10).

Chainey et al. (8,9) have carried out surfactant-free emulsion polymerisation using both seeded-growth and shot-growth processes to overcoat polystyrene latex particles with polymethylmethacrylate, polymethylacrylate, polyethylacrylate, polybutylacrylate and polybutylmethacrylate. They claim that the acrylate coat is more strongly bound to the polystyrene particles using the shot-growth method than using the seeded-growth method. These authors report that neither process produced a monodispersed overcoated latex particles when ethylacrylate was used as the coating monomer.

The shot-growth process has been investigated by Sakota and Okaya (10) with regard to the efficiency of incorporation of carboxyl groups on the surface of styrene/isoprene copolymer latices. They found that 60% of the polymerised carboxylic acid groups were combined at the surface of the latex particles if the carboxylic acid was added at 80% conversion of the styrene/isoprene, and that this proportion was increased to 80% if the addition of the carboxylic acid was delayed until the styrene/isoprene was 95% polymerised. It should be noted that carboxylated (and other functional-group) latices are

a very special type of core-shell latex - thus, for example, the "shell" is usually extremely thin.

It should be pointed out that, although any given process might be expected to give a latex containing core-shell particles, this is no guarantee that in fact the process does give core-shell particle, or that if it does, the core and shell are as expected rather than inverted. It should also be noted that there are sophisticated variants of the three basic methods discussed above, in particular, the so-called "power-feed" process (11) for producing latex particles which have (supposedly) graded composition.

3.3 Mechanism of core-shell emulsion polymerisation

Chainey *et al.* (9) have studied the mechanism of the formation of core-shell particle during the aqueous emulsion polymerisation of various acrylates on polystyrene latex seeds. These authors have argued that the locus of polymerisation of the coating monomer is likely to be at the particle/water interface, where the residual styrene will polymerise within the core. However, consideration has to be given to the fact that a large amount of the monomer is dispersed as droplets in the aqueous phase, and its behaviour there will strongly influence the outcome of the reaction. The solubilities in water, and rates of polymerisation of acrylate monomers are greater than those of styrene. Both these factors will facilitate the formation of oligomeric radicals within the aqueous phase. These oligomeric radicals would normally be expected to micellise or coagulate to form loci for the growth of secondary latex particles. This did not occur, and the authors attribute this to a high capture effciency of the core particles. It was also suggested that the high capture efficiency was due to the shell monomer polymerising at the particle/water interface, thereby becoming covalently bound to the core particle and unable to transfer from the particles into the aqueous phase.

Fig. 3.1 SEM of fracture cross section of film cast from latex prepared by short-growth process. Magnification ×6,165 (9)

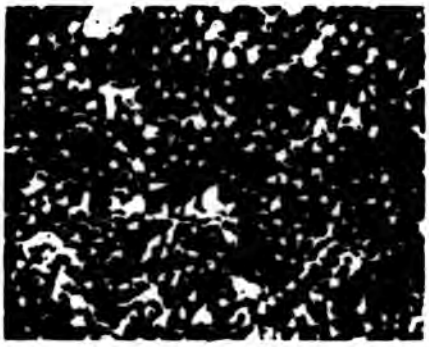


Fig. 3.2 SEM of fractured cross section of film cast from latex prepared by seeded-growth process. Magnification ×6,165 (9)

Evidence for polymerisation of acrylate monomer units by interaction with free radicals at the surface of the core particles was obtained from a comparison of scanning electron micrographs of films cast from the overcoated latices prepared by both shot-growth and seeded-growth methods. It was reported that covalent combination of the coating polymer to the core particles occurs in the shot-growth process, as is demonstrated by the retention of acrylate polymer on the core particles. This is demonstrated in Figure 3.1 which shows the fracture surface at room temperature of a film cast from a latex prepared by the shot-growth process. There is a clear contrast between the polystyrene core particles (dark) and the polyacrylate coat (light) which, according to the authors, has presumably been stripped off the polystyrene core and then collapsed back on fracture. The small globules adhering to the core particles have been interpreted as polyacrylate material covalently combined to the surface of the core particles. Chainey et al. have also argued that such combination does not occur during the seeded-growth processes. This is demonstrated in Figure 3.2, which shows fracture at room temperature of a film cast from latex prepared by the seeded-growth process. This fracture surface reveals that the acrylate coat has separated from the underlying seed particles. None of the exposed core particles shows the small globules of acrylate polymer.

Stutman et al. (12) have also studied the mechanism of core-shell emulsion polymerisation. The polyacrylate seed/polystyrene shell system was chosen for this investigation because of the known anomalous behaviour of this system. Twelve operator-controllable variables were chosen for the investigation. These authors have found that alteration of the twelve process variables produced a large change in the morphology of the resulting particles. Changes observed included (I) the production of a second generation of particles, (II) the production of polystyrene domains, (III) changes in the amount of

grafting, and (IV) changes in the average thickness and coherence of the ultimate polystyrene shell. This comprehensive investigation has led the authors to propose that aqueous-phase polymerisation leads to the formation of secondary polystyrene particles, and that the mechanism of core-shell emulsion polymerisation involves a balance between capture of the newly-nucleated particles and polymerisation in a polybutylacrylate particle surface layer which is rich in monomer.

Williams et al. (13,14) have reported that the kinetics of styrene emulsion polymerisation can be explained by assuming that the presence of styrene/polystyrene particles in the reaction system. These authors have presented a heterogeneous model for monomer-polymer particles which are present in the reaction system for the emulsion polymerisation of styrene. In this model, the growing particle consists of an expanding polymer-rich (monomer-starved) core surrounded by monomer-rich (polymer-starved) spherical shell. The outer shell serves as the major locus of polymerisation, whilst virtually no polymerisation occurs in the core because of its monomer-starved condition. The authors claim that the core-shell model was suggested by kinetic data involving the measurement of the particle monomer concentration during the process of the reaction, the measurement of rates of polymerisation, and initiator perturbation studies. The main point about the hypothesis of Williams et al. is that they suggest that even conventional emulsion polymerisation reaction may in fact proceed in what are effectively core-shell particles. It should be pointed out that the idea of Williams et al. concerning this matter are now largely discredited - the criticism of Gordon (15) sited below is one of several (15 - 17).

Gordon (15) has expressed certain reservations concerning the appilcability of the core-shell model to styrene emulsion polymerisation as presented by Grancio and Williams, and also concerning the encapsulated model

for monomer saturated polystyrene latex particles proposed by Keush and Williams. Gordon has argued that the core-shell model proposed by these workers is inconsistent with the theory of Smith and Ewart and others (17). He also pointed out the arguments that have been advocated by Williams and others were based on conversion data which were thought to be linear with time whilst a re-examination of these data indicates that they are not. But, in any event, the particles which are produced at the end of a conventional emusion polymerisation reaction are generally believed to be homogeneous, notwithstanding that they might possibly have been heterogeneous at some stage during the reaction.

In summary, the various studies which have been carried out on the mechanism of emulsion polymerisation reactions that lead to the formation of core-shell latex particles have indicated that the major locus for the polymerisation of the shell monomer may be in the aqueous phase. Such aqueous-phase polymerisation inevitably tends to lead to the formation of secondary particles of shell polymer, and the polymerisation mechanism involves a balance between the capture of newly-nucleated particles and polymerisation in the core polymer particle surface layer.

3.4 Morphology of core-shell latex particles

The morphology of latex particles produced by seeded-growth emulsion polymerisation has been extensively studied by many investigators (9,18-22). This subject has recently been reviewed by Eliseeva (23). From the literature survey carried out by the present author, the following principles emerge concerning the morphology of two-stage latex particles polymerised in aqueous medium with monomer or monomer mix II in the presence of polymer seed I (which may be either a homopolymer or a copolymer) : (I) If polymer I is insoluble in monomer II, then polymer II will form surface layers like "onion skin",

e.g., poly-vinylidene chloride/polymethylacrylate, etc. (II) If polymer II is miscible with polymer I and there is no difference in hydrophilicity between them, then a polymer II-rich outside layer will be formed, resulting in core-shell latices, e.g., polystyrene/polystyrene, polymethylacrylate/polyethylmethacrylate, etc. (III) If monomer II swells polymer I, but polymer II is immiscible with polymer I, phase separation can take place and many different structures are possible, e.g., polyethylacrylate/polystyrene, polystyrene/styrene-butadiene copolymers etc. (IV) If polymer I is crosslinked and is immiscible with polymer II, polymer II can be trapped within polymer I to form two interpenetrating, continuous phases which are surrounded by a shell which is rich in polymer II. (V) If polymer II is more hydrophilic than polymer I, polymer II tends to form a core-shell structure with polymer II as the shell. The present section describes some of the studies that have been carried out concerning the morphology of core-shell latex particles produced by emulsion polymerisation in relation to these principles.

As has already been noted, Chainey et al. (8) have successfully overcoated polystyrene particles with a range of acrylate polymers. Markis (18) has observed that changing the sequence of seed latex and monomer introdution (i.e., adding styrene to a polyacrylate seed latex) did not alter the morphology of the core-shell polymer particles. The intension is to compare this with the product obtained by polymerising the acrylate monomer in a polystyrene latex. Thus the styrene added to a polyacrylate seed latex enters the particles, polymerises, phase separates and forms a polystyrene domain within soft polyacrylate particles, rather than forming external hard polystyrene shells. This is due to the fact that polystyrene is more hydrophobic than the acrylate polymer. This effect has also been studied by Lee and Ishikawa (19) as discussed below.

Lee and Ishikawa (19) have demonstrated that the

determining factor in forming particles having core-shell morphology is the hydrophilicity of the core and shell polymers and that in two-stage polymerisation the shell is always composed of the more hydrophilic polymer. These conclusions were reached from evidence obtained by electron microscope observation, surface acid titration and surface reactivity. They observed that, when hydrophobic monomers such as styrene and styrene/butadiene were polymerised in the presence of highly hydrophilic polymer seed particles, such as copolymers of ethylacrylate and methacrylic acid, the second-stage hydrophobic polymers separated and formed cores surrounded by the first-stage hydrophilic polymers, resulting in "inverted" core-shell - latices. Figure 3.3 represents schematically the morphology of latex particles produced by the two-stage emulsion polymerisation of hydrophilic (I) and hydrophobic (II) monomer. It shows the domain structure and inverted core-shell morphology which Lee and Ishikawa propose is formed.

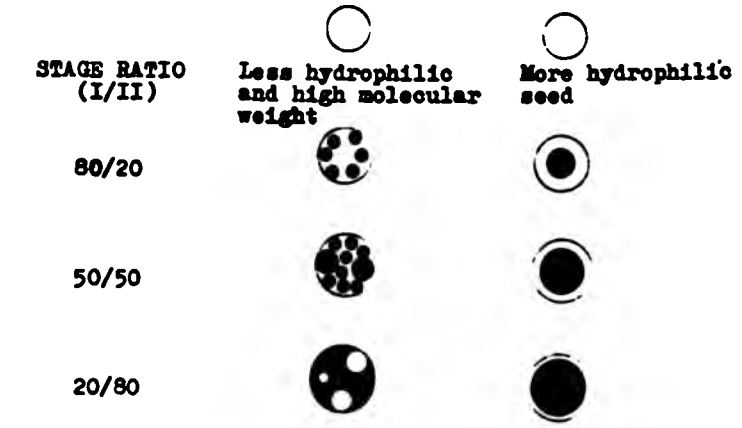


Fig. 3.3 Morphology of two-stage (hydrohilic I/hydrophobic II) latex particles : light region, hydrophilic polymer I; dark region, hydrophobic polymer (II) (19)

Muroi et al. (20) have investigated the morphology of the particle contained in two types of carboxylated seed latices. In the first, a methylacrylate/methacrylic acid (90/10) mixture was polymerised on a polyethylacrylate/methacrylic acid (90/10) latex. In the second, an ethylacrylate/methacrylic acid (90/10) mixture was polymerised in a polymethylacrylate/methacrylic acid (90/10) latex. It was shown that the shell of the particles of both latices contained polymethylacrylate/methacrylic acid molecules which were relatively rich in methacrylic acid, and that, in both cases, the core contained both polymethylacrylate /methacrylic acid and polyethylacrylate/methacrylic acid molecules. Thus morphologies of the particles of the composite polymers investigated were virtually identical irrespective of the manner in which the methylacrylate and ethylacrylate were brought together in the first and second stages of the process. In both cases, the more hydrophilic polymer was always found in the shell. This is in accordance with the results obtained by Lee and Ishikawa (19).

Okubo et al. (21,22)) have studied the polymerisation of styrene in polymethylmethacrylate and polymethylacrylate seed latices. They have shown that the polystyrene molecules phase-separate and form domains in polymethylmethacrylate and polymethacrylate particles. These authors have also reported that polystyrene molecules can form domains more readily in the polymethylacrylate/polystyrene systems than in the polymethylmethacrylate/polystyrene systems, because polymethylacrylate is more hydrophilic and also more flexible than is polymethylmethacrylate.

CHAPTER FOUR : EXPERIMENTAL

4.1 Materials

(a) Rubber latices

The natural rubber latex used was a low-ammonia concentrate supplied by LRC Products Ltd.. The latex was used as received without modification. The characterisation data for the latex are given in Table 4.8 (Section 4.3.2).

The styrene-butadiene (24/76) rubber latex used was a concentrate of the Intex 132 type which is made using the pressure-agglomeration process. The latex was supplied by Enichem Elastomers Ltd., and was used as received. The characterisation data for the latex are given in Table 4.8 (Section 4.3.2).

The acrylonitrile-butadiene (32/68) rubber latex used was a Breon 1562 type. The stabilisation system is said to be based on a synthetic anionic surfactant. The latex was supplied by British Petroleum Company, and was used as received. The characterisation data for the latex are given in Table 4.8 (Section 4.3.2).

(b) Monomers

Styrene and α-methylstyrene - 99% pure, inhibited with 10-15 ppm p-tert-butylcatechol, were supplied by Aldrich Chemical Ltd., and were used as received.

Methylmethacrylate - 99% pure, inhibited with 65 ppm MEHQ, was supplied by Aldrich Chemical Ltd., and was used as received.

Acenaphthylene - a crystalline solid, 95% pure, was supplied by Aldrich Chemical Ltd., and was used as received.

Structure of acenaphthylene :

Butylacrylate - minimum purity 99%, inhibited with 15-50 ppm MEHQ, was supplied by Aldrich Chemical Ltd., and was used as received.

Dodecylacrylate - 60-70% pure (30-40% longer hydrocarbon chain (C_{13}-C_{18})), was supplied by Fluka, and was used as received.

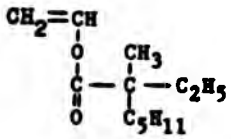
Dodecylmethacrylate - minimum purity 95%, inhibited with 0.01% hydroquinone monomethyl ether, was supplied by Fluka, and was used as received.

Octadecylmethacrylate - minimum purity 95%, inhibited with 0.01% hydroquinone monomethyl ether, was supplied by Phase Separations Ltd., and was used as received.

Isoprene - minimum purity 99%, inhibited with p-tert-butylcatechol, was supplied by Fluka, and was used as received.

Allylmethacrylate - minimum purity 98%, inhibited with 0.6% hydroquinone, was supplied by Fluka, and was used as received.

VeoVa 10 - vinyl ester of a synthetic saturated monocarboxylic acid mixture of highly-branched C-10 isomers, minimum purity 95%, inhibited with 3-7 ppm hydroquinone monomethyl ether, was supplied by Shell Chemicals U.K. Ltd., and was used as received.
The structure of the main component of VeoVa 10 is :



Ethylene-glycol dimethacrylate - 98% pure, was supplied by Fluka, and was used as received.

Divinylbenzene - 50-60% w/w in ethyl vinylbenzene, inhibited with 0.1% tert-butylcatechol, was supplied by Aldrich Chemical Ltd.. It was purified by washing twice with 10% (w/v) sodium hydroxide solution, and twice with distilled water, followed by separation and drying with anhydrous potassium carbonate.

(c) Other polymerisation reagents

Potassium persulphate - minimum purity 99%, was supplied by Aldrich Chemical Ltd., and was used as received.

Potassium myristate - was prepared using potassium hydroxide (Aldrich Chemical Ltd.) and myristic acid (Aldrich Chemical Ltd.) according to the following reaction :

$$C_{13}H_{27}COOH + KOH \rightarrow C_{13}H_{27}COOK + H_2O$$

The following procedure was used: The calculated amount of myristic acid required to produce 200g of 10% aqueous potassium myristate solution was accurately weighed into pre-weighed bottle (250ml). About 80g of distilled water was added to the myristic acid. The contents of the bottle were warmed to about 60°C in a thermostatically-heated water bath. The required amount of potassium hydroxide was added as a 10% aqueous solution into the warmed myristic acid, and the temperature was maintained at 60°C for a further 30 minutes under constant stirring. More potassium hydroxide solution was added until the pH of the soap solution was $\triangleq$ 10.5. Potassium hydroxide solution having pH $\triangleq$ 10.5, i.e., 3.2×10^{-4}M was then added until the weight of the soap solution was 200g. If required, these soap solutions were diluted with potassium hydroxide solution having pH $\triangleq$ 10.5 to the appropriate concentration required for the experimental work.

Sodium bisulphite - minimum purity 97%, was supplied

by Aldrich Chemical Ltd., and was used as received.

(d) Vulcanising ingredients

Sulphur, zinc diethyldithiocarbamate (ZDC), zinc oxide, stearic acid and antioxidant 2246 (2,2'-methylene bis(4-methyl-6-tert-butyl phenol)) were supplied by Anchor Chemical Ltd., and were used as received.

(e) Dispersing agent, stabiliser and viscosity modifiers used for preparing dispersion for vulcanising ingredients

A common dispersing agent, the disodium salt of methylene di-naphthlene sulphonic acid (Dispersol LN), was used. An ethylene-fatty acid alcohol adduct (Vulcastab LW) was used as stabiliser. Methyl cellulose was used as the viscosity modifier. Dispersol LN and Vulcastab LW were supplied by ICI Ltd., and were used as received. Methyl cellulose was supplied by Courtaulds Chemical and Plastics Company, and was used as received.

(f) Carbon black (SAF) - was supplied by Philips Petroleum, and was used as received.

(g) Natural rubber (Smoked sheet) - was supplied by MRPRA

(h) Other material : All other materials used, e.g., calcium chloride, calcium nitrate, toluene, acetone, methanol and industrial methylated spirit, were of analytical-reagent grade wherever possible.

4.2 Preparation of filler latices

The polymeric filler particles were prepared as latices by emulsion polymerisation. With the exception of latices containing rigid particles whose surfaces were to be functionalised with polyisoprene (Section 4.2.6.2). The

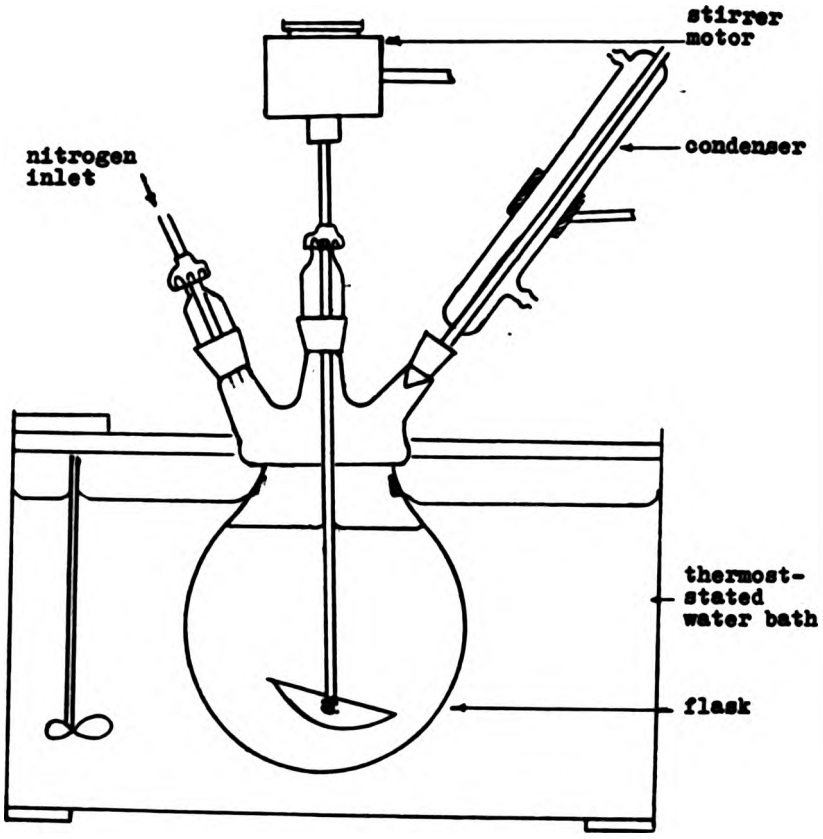


Fig. 4.1 Apparatus for carrying out emulsion polymerisation reactions

emulsion polymerisation reactions were carried out in a one-litre, three-necked, round-bottomed flask, equipped with a double-walled condenser, nitrogen inlet and outlet, and stirrer, as shown in Figure 4.1. The polymerisation temperature was controlled within specified limits by means of a thermostated water bath. During the entire course of the polymerisation, the reaction flask was kept under a positive pressure of 3cm water height of oxygen-free nitrogen. The rate of bubbling of nitrogen was controlled at about 25 bubbles per minute.

4.2.1 Preparation of latices containing rigid particles of small sizes (40 - 70nm)

Polystyrene, polymethylmethacrylate, poly α-methylstyrene and polyacenaphthylene latices were prepared by conventional emulsion polymerisation according to the recipes shown in Table 4.1. The procedure for carrying out an emulsion polymerisation was as follows: The emulsifier was made up as 10% aqueous solution. The initiator was made up of 5% aqueous solution. All the reaction mixtures were charged from the beginning into the reaction flask, which was kept in a thermostated water bath. Nitrogen was bubbled in vigorously for the first five minutes and subsequently at a controlled rate of 25 bubbles per minute.

Styrene and methylmethacrylate were polymerised at 60°C for 3½ hours, giving 98-99% conversion. The particle size of the resultant latices were found to be 68 and 69nm respectively. Polystyrene and polymethylmethacrylate of small particle sizes (40-50nm) were prepared using higher levels of soap and initiator at 80°C (see Table 4.2). The latices were vacuum stripped to remove residual monomer. Acenaphthylene was polymerised at 50°C for 24 hours. The final latex was greenish-yellow, the conversion being 88%. The residual monomer was removed by precipitation. This was done by allowing the latex to stand overnight and the precipitated monomer, which remained as a crystalline

Table 4.1 Polymerisation recipes and results for latices containing rigid particles

Ingredient	Parts by weight			
	PS	PMMA	PAcN	PαMS
Styrene	100	-	-	-
Methylmethacrylate	-	100	-	-
Acenaphthylene	-	-	100	
α-Methylstyrene	-	-	-	100
Water	200	200	900	200
Potassium myristate	5.0	5.0	20	5.0
Potassium persulphate	0.5	0.5	1.6	0.7-2.8
Sodium bisulphite	-	-	-	0.5-2.0
Polymerisation temp. (°C)	60	60	50	25
Polymerisation time (hr.)	3.5	3.5	24	6-26
Total solids content (%)	33.9	34.4	8.22	8.9-10.6
Conversion (%)	98.2	99.6	88.0	210-22.9
Particle size (nm)				
Turbidity method	71	70	120	-
Coulter Nano sizer	68	69	100	-
Surface tension at 20°C (mNm^{-1})	57.3	43.5	52.0	-
pH at 20°C	10.1	9.6	11.8	-

PAcN - polyacenaphthylene

PαMS - poly α-methylstyrene

Table 4.2 Typical polymerisation recipes and results for latices containing small rigid particles

Ingredient	Parts by weight	
	PS	PMMA
Styrene	100	-
Methylmethacrylate	-	100
Water	1000	1000
Potassium persulphate	2.0	2.0
Potassium myristate	6.7	6.7
Polymerisation temp. (^{o}C)	80	80
Polymerisation time (hr)	3.5	3.5
Total solids content (%)	9.4	9.6
Conversion (%)	95.5	97.7
Particle size (nm)	35-56	44-100
Surface tension at 20^{o}C (mNm^{-1})	57.7	40.5
pH at 20^{o}C	8.4	8.6

solid throughout the emulsion polymerisation, was separated from the latex by filtration the following day. α-Methylstyrene was polymerised for 25 hours at 25°C (below its ceiling temperature which is reported to be 61°C (1)). This reaction yielded 22% conversion to polymer. Further experiments with this monomer, in which recipes and condition of polymerisation were varied considerably, did not increase the overall conversion to polymer to a level which would be commercially acceptable (2). For this reason , the polymer was not used in the present work.

4.2.2 Preparation of latices containing rigid particles of large sizes (100-500nm)

Of the various methods (3-6) available for preparing monodispersed latices of large size, the seeded-growth technique was thought to be the most suitable for synthesising the polystyrene and polymethylmethacrylate particles required for investigation of the effect of filler particle size upon the reinforcement of dried films derived from natural rubber latex.

For the preparation of the initial seeds, conventional emulsion polymerisation was used. For seeded-growth polymerisation, the emulsifier content and particle size of the seed latex must be known. From this information, the amount of emulsifier required for the next step can be determined. Appendix A shows a typical calculation for the amount of emulsifier and monomer to be added for each step of seeding, in order to ensure that no nucleation of new particles occurs and that a stable latex is obtained. The calculated amount of soap and monomer were first added to the seed latex at 25°C, and the mixture was then stirred at moderate speed (250rpm) for about one hour or so to permit attainment of equilibrum. The initiator was not added at this stage because of the risk of polymerisation occurring within the soap micelles which had not yet dissociated and adsorbed at the particle

Table 4.3 Typical polymerisation recipes and results for seed latices prepared by emulsion polymerisation

Latex No.	1	11	111	1V	V	V1	V11	V111	1X
Seeded with latex No.	None	1	11	111	1V	V	V1	V11	V111
Parts of seed latex	None	40	40	40	40	40	40	40	40
Parts of seed polymer	None	12.8	8.4	8.8	11.2	11.8	11.4	13.2	13.5
Styrene	100	23	15	15	20	20	17	18	19
Potassium persulphate	0.5	0.25	0.16	0.16	0.2	0.2	0.15	0.15	0.15
Potassium myristate	5.0	0.70	0.35	0.29	0.28	0.23	0.16	0.14	0.13
Water	200	100	50	28	44	45	28	35	37
Polymerisation temp. (^{o}C)	60	60	60	60	60	60	60	60	60
Polymerisation time (hr.)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Conversion (%)	97.8	96.5	99.0	98.1	99.2	98.3	98.8	98.2	98.5
Particle size (nm)	70	92	124	157	200	275	350	420	500
Polydispersity index *	2	1	0.6	1	0.5	0	0.4	0	0

* see section 4.3.1.1 for definition

Table 4.4 Polymerisation recipes and results for latices containing crosslinked particles

Ingredients	Parts by weight	
	PS(XL)	PMMA(XL)
Styrene	100	-
Methylmethacrylate	-	100
Divinyl benzene	0.5-5.0	-
Ethylene-glycol dimethacrylate	-	0.5-5.0
Water	200	200
Potassium myristate	5.0	5.0
Potassium persulphate	0.5	0.5
Polymerisation temp. (^{o}C)	60	60
Polymerisation time (hr.)	3.5	3.5
Total solids content (%)	33.8-35.0	34.2-35.5
Conversion (%)	97.5-98.5	98.7-99.4
Particle size (nm)	69-74	70-74
Surface tension at 20^{o}C (mNm^{-1})	53.0-54.0	41.0-42.0
pH at 20^{o}C	10.0	9.8

surfaces. After equilibrum was attained, the initiator solution was added to the reaction flask, and the polymerisation was carried out by raising the temperature of the flask to 60°C. The polymerisation was carried out under nitrogen atmosphere, as described for the conventional emulsion polymerisations. The polymerisation time was 3½ hours for each step. Table 4.3 gives some typical recipes and results for seed latices prepared in the present work.

4.2.3 Preparation of latices containing crosslinked particles

Crosslinked polystyrene and polymethylmethacrylate particles were prepared by conventional emulsion polymerisation at 60°C for 3½ hours leading to 97-99% conversion. The crosslinking agents were divinylbenzene and ethylene-glycol dimethyacrylate respectively. The levels of crosslinking agent were varied between 0.5 and 5.0 parts per hundred monomer (Table 4.4).

4.2.4 Preparation of latices containing core-shell particles

A variety of methods (7-9) have been used for preparing copolymer latices of given overall composition but having different morphologies such as uniform copolymer, core-shell and gradient copolymer. As has already been noted in Chapter 3 (Section 3.2), these methods fall essentially into three categories : (a) the "conventional" process, where the comonomers are both charged at start of the reaction; (b) the "seeded-growth" process, where the second monomer is added to core latex which is already completely polymerised; (c) the "shot-growth" process, which is a compromise between the previous two approaches, where the seed latex is allowed to reach a fairly high conversion (>60%) before the second monomer is added.

In the present investigation, both seeded-growth and shot-growth methods were used to overcoat polystyrene latex particles with polybutylacrylate, polydodecylacrylate, polydodecylmethacrylate and polyVeoVa 10. The conventional method was used to prepare random copolymers of styrene and butylacrylate. The polymerisation recipes for these latices are summarised in Tables 4.5 and 4.6. The seeded-growth and shot-growth techniques were expected to give particles having a core-shell structure consisting of a polystyrene-rich inner core and outer shell rich in the second polymer. For particles produced by the shot-growth method, the polymer coat was expected to be more strongly bound to the core particles than was the case for particles produced by the seeded-growth method. In the case of the conventional method, a latex whose particles contain a uniform copolymer of styrene and the acrylate monomer is expected to be formed. The uniformity of the mixture at the molcular level will depend upon the monomer reactivity ratios of the comonomers. The polymerisation reactions were carried out as follows :

(a) Conventional method

The styrene and the second monomer were copolymerised in the reaction flask simultaneously by the conventional method outlined in Section 4.2.1.

(b) Seeded-growth method

Polystyrene seed latex was prepared by conventional emulsion polymerisation. The seed latex, the second monomer and water (if necessary) were added in the flask and stirred for 2 hours at 25°C. The initiator and the soap solutions were then added and the polymerisation carried out at 60°C as before.

Attempts were also made to prepare core-shell latices which contained particles having soft cores and hard

Table 4.5 Polymerisation recipes for preparing copolymer latices of styrene and a range of acrylate monomers and VeoVa 10

Ingredient	Parts by weight
Monomers	100
Water	200
Potassium myristate	4.5
Potassium persulphate	0.5
Polymerisation temp. (^{o}C)	60
Polymerisation time (hr.)	3.0-4.5

Table 4.6 Ratio of comonomers

	Parts by weight				
Monomer 1	90	80	70	60	50
Monomer 11	10	20	30	40	50

Monomer 1 : styrene
Monomer 11 : a range of acrylate monomers and VeoVa 10

Table 4.7 Typical properties of copolymer latices of styrene and butylacrylate prepared in various ways

Latex	Surface tension mNm^{-1}	pH	Core size nm	Core-shell size nm	Conversion %
CON 10	52.8	10.6	74.3	-	98.8
SE 10	47.8	9.80	72.0	74.6	99.9
SH 10	48.5	9.70	69.5	72.5	99.9
INV 10	42.5	10.0	84.0	88.5	99.1
CON 20	48.5	9.70	73.0	-	99.0
SE 20	46.2	9.93	72.0	77.6	98.5
SH20	45.0	9.02	64.0	68.5	99.0
CON 30	50.0	9.68	74.0	-	99.6
SE 30	44.5	9.81	72.0	81.1	99.9
SH 30	44.0	9.15	64.9	71.5	99.3
INV 30	35.5	9.50	84.0	91.1	98.9
CON 40	47.7	9.61	76.5	-	98.1
SE 40	43.9	9.90	72.0	85.3	98.7
SH 40	45.0	9.66	60.0	70.0	98.0
CON 50	47.3	9.48	74.0	-	97.8
SE 50	41.9	9.98	72.0	90.7	98.5
SH 50	43.5	9.65	63.0	78.0	99.4
INV 50	37.2	10.1	84.0	92.9	98.7
PS seed	58.0	10.1	72.0	-	99.8
PBA seed	43.8	9.36	76.0	-	99.5

Codes used:

CON 10 - CON 50 : CON indicates Conventional emulsion polymerisation; the number indicates the parts by weight of butylacrylate

SE and SH indicate Seeded-growth and Shot-growth processes respectively

INV indicates copolymer latices prepared by SE which were thought to contain particles having "inverted" core-shell morphology

shells by polymerising styrene in a polybutylacrylate seed latex particles. However, it is believed that this polymerisation resulted in the formation of particles having an "inverted" core-shell morphology, because of the occurrence of phase inversion (Section 3.4).

(c) Shot-growth method

The polymerisation of styrene was first initiated at 60°C and allowed to proceed to fairly high conversion (about 80%) by the conventional method. The second monomer was then added dropwise at the rate of about 0.1ml per minute. Thus most of the polymerisation of the styrene occurred before that of the second monomer.

Typical properties of copolymer latices prepared by these methods (i.e., conventional, seeded-growth and shot-growth) are given in Table 4.7.

4.2.5 Preparation of latices containing core-shell particles using a "linker"

The shot-growth method was used to prepare core-shell polymer latices of this type. It was expected that the "linker", allylmethacrylate would copolymerise with the core monomer through the methacrylate group, since this is much more reactive than the allyl group. This would produce a core containing unreacted allyl group which may then copolymerise with the shell monomer. As a consequence, allylmethacrylate was expected to promote the formation of covalent linkages between the core polymer and the shell polymer. The core monomer used in this investigation was styrene, and the shell monomers were dodecylacrylate and VeoVa 10.

For this reaction. the polymerisation of styrene was first initiated at 60°C and allowed to proceed to about 80% conversion as before. Allylmethacrylate was then added dropwise at the rate of about 0.1ml per minute . When all

the allylmethacrylate had been added, the reaction was allowed to proceed to completion. The polymer contained in the resulting latex was expected to contain unreacted carbon-carbon double bonds. This was confirmed by determining the amount of unsaturation in the latex using Wijs' method (Section 4.3.1.7). The latex was then allowed to cool to 25°C and the second monomer added. The mixture was stirred for 2 hours. The initiator and soap solutions were then added and the polymerisation carried out at 60°C as described previously.

4.2.6 Preparation of latices containing rigid particles whose surfaces have been functionalised to make them co-vulcanisable with the rubber matrix

Attempts were made to promote chemical interaction between the surface of the filler particles and rubber matrix in which they were embedded by functionalising the surface of the filler particles in various ways to make them co-vulcanisable with the rubber matrix. This aspect of the investigation was carried out using polystyrene particles as the filler and allylmethacrylate and isoprene as the functional monomers. It was expected that the resulting copolymer would contain unreacted carbon-carbon double bonds and α-methylene hydrogen atoms which subsequently could cause the molecules of the filler particles to co-vulcanise with, for example, natural rubber during the sulphur vulcanisation reaction.

4.2.6.1 Preparation of polystyrene latex particles functionalised with allylmethacrylate units

The polymer latices were prepared by the shot-growth method which involved the polymerisation of styrene at 60°C to about 80% conversion, followed by the dropwise addition of allylmethacrylate at the rate of about 0.1ml per minute. In order to investigate the combined effect of physical interaction by mixing and chemical interaction,

Table 4.8 Polymerisation recipes for preparing latices containing particles whose surfaces were functionalised

Ingredient	Parts by weight	
	PS/PAMA	PS/PI
Styrene	100-50	100-50
Allylmethacrylate	0-50	-
Isoprene	-	0-50
Water	200	250
Potassium myristate	4.5	5.0
Potassium persulphate	0.5	0.5
Polymerisation temp. (^{o}C)	60	60
Polymerisation time (hr.)	3.5	4.0
Conversion (%)	98.5-99.5	98.5-96.0
Particle size (nm)	72-90	72-92
Surface tension at 20^{o}C (mNm^{-1})	58.5-35.1	58.5-50.0
pH at 20^{o}C	10.1-9.7	10.1-9.8

the polystyrene particles were overcoated with a mixture of both polyallylmethacrylate and polydodecylacrylate by the shot-growth technique. The polymerisation recipes are given in Table 4.8.

4.2.6.2 Preparation of polystyrene latex particles functionalised with isoprene units

The seeded-growth emulsion polymerisation method was used. Because of the volatility of isoprene, the polymerisations were carried out in 175-ml beverage bottles in a thermostated water bath. The polystyrene latex was prepared by conventional emulsion polymerisation. The empty bottle was first purged with nitrogen gas for a few minutes. The seed latex, isoprene monomer and water were then placed in the bottle, quickly sealed with a screw cap lined with polyethylene terephthalate, and then rotated at 60rpm for 2 hours at 20°C to permit attainment of equilibrum. After equilibrum was attained, the screw cap was removed and the required amount of initiator (potassium persulphate) and soap (potassium myristate) solutions were quickly added to the bottle, and the bottle then quickly sealed as before. Polymerisations were carried out at 60°C. No leakage was detected from the bottles. This was checked by weighing the bottles. The polymerisation recipes are given in Table 4.8.

4.3 Characterisation of polymer latices

4.3.1 Characterisation of filler latices

4.3.1.1 Determination of particle size

The particle size of the filler latices were determined using a Coulter nano-sizer. The instrument detects changes in the scattered light as particles vibrate under the influence of Brownian motion, and by

analysis of the particle motion calculates the average particle size. Since the instrument measures the diffraction of all the particles, and not that of individual particles, it is not possible to obtain the particle-size distribution as well, but the instrument does compute and present a so-called "polydispersity index". This index, which ranges from 0 to 9, is an arbitrary measure of the width of the size distribution. For instance, an index of 0 to 1 indicates an essentially monodispersed distribution, whereas 8 to 9 indicates broad distribution of particle sizes.

The determination of latex particle size by Coulter nano-sizer was straightforward. A diluted latex sample, e.g., one drop of original latex in 150ml of distilled water, was placed in the sample compartment. The average diameter of the latex particles and the polydispersity index were displayed by the instrument in 2 to 4 minutes.

Initially, the turbidity method (10) was also used to determine the particle sizes of the filler latices. However, the values obtained using this method and Coulter nano-sizer were similar within experimental error as given in Table 4.1 (Section 4.2.1). Hence the Coulter nano-sizer was the preferred method because it was quicker.

4.3.1.2 Examination of particle size distribution and shape by electron microscope

An electron microscope was used to obtain information on the shape and size ditribution of the various filler particles. The particles in a latex to be studied by electron microscope should be sufficiently rigid to resist collapse. Since the filler particles were sufficiently rigid in themselves, no hardening was necessary. However, the polystyrene particles overcoated with thick coats of acrylate polymers were hardened by osmium tetroxide. For each latex sample, two dilutions (1-2 drops of latex in 200ml of distilled water) were used. One drop of osmium tetroxide solution was added to the diluted latex sample

containing overcoated polystyrene particles. A drop of the diluted latex was placed on a 200-mesh copper grid coated with Formvar support film, and allowed to dry at room temperature. The support film was made by casting a 0.3% solution of Formvar in ethylene dichloride on a glass slide from which it was then transfered to 200-mesh copper grids - which served as the mount for the latex specimens. Electron micrographs were obtained using a transmission electron microscope (AEI EM6G).

4.3.1.3 Measurement of surface tension

The surface tensions of the air/water interfaces of the filler latices were determined at 20°C using a Du Nouy surface tension apparatus according to the procedure specified in BS 4561 : 1970. For each latex, three determinations were made, and the average value taken.

4.3.1.4 Determination of pH

The pH of each latex was measured using a Philips digital pH meter type PW 9409. Measurements were made at a temperature of 20 ± 1°C.

4.3.1.5 Determination of total solids content

About 2-3g of the latex were weighed into a dish covered with a lid, and dried to constant weight at 100°C in an oven. Prior to drying, one or two drops of hydroquinone solution were added to the latex to prevent further polymerisation of the residual monomer. The percentage of total solids (TSC) is defined as

$$TSC = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100$$

The fractional conversion during emulsion polymerisation

is the difference between the percent TSC and the percent non-polymeric solids all divided by the theoretical percent polymer solids for full conversion. The non-polymeric solids here are surfactants and initiator residues.

4.3.1.6 Investigation of morphology of core-shell latex particles

The first matter that needs to be considered in the investigation of the morphology of core-shell latex particles is that of initial and final particle size. One needs to know whether or not the ratio (final diameter:initial diameter) is approximately that expected for the formation of core-shell particles. If it is significantly less, then this indicates that new particles were formed during the overcoating process. Under this circumstance one would expect an increased polydispersity. On the other hand if the ratio is significantly higher, then this indicates that particle agglomeration has occurred during the overcoating process. In the present work, it was found that, as given in Table 4.7, the initial and final particle sizes are consistent with core-shell having been formed. However, it must be realised that the expected size increase does not prove the formation of core-shell particles and it says nothing about the structure of the particles. But if the size increase is not as expected, then one has clear indication that the overcoating reaction did not proceed as expected. In this connection, in addition to particle size measurement, various methods have been used in order to gain some indication of the morphology of the core-shell latex particles prepared in the present work. These methods include surface tension measurement and electron microscopic examination.

(A) Surface tension method

The surface tensions of the core-shell latices and of

their blends with natural rubber latex were determined in order to obtain some indication of the structure of the overcoated particles. It was expected that, if the rigid polystyrene core were completely overcoated with the acrylate polymer, the surface tension of the core-shell latex would be similar to that of the acrylate polymer, as polystyrene and acrylate polymer latices have been found in the present work to have different surface tensions, even though the polymer contents, soap contents and particle sizes were similar. For instance, typical surface tensions of polystyrene and polybutylacrylate latices were 58.0 mNm^{-1} and 43.8 mNm^{-1} respectively. If the surface tension of latices of similar polymer contents and particle sizes do differ significantly, then this presumably is a conequence of differences in the saturation adsorption areas of the soap molecules at the surfaces of the particles.

The surface tension measurements were carried out at 20°C using the Du Nouy method.

(B) Electron microscopy method

In order to obtain further indications of the morphology of the core-shell latex particles, the ruptured surfaces of films cast from the latices containing polystyrene particles overcoated with a range of acrylate polymers were examined by a scanning electron microscope (Hitachi S450). Prior to examination, the ruptured surfaces were coated with gold. This was achieved by evaporation of the metal on the ruptured surface in vacuum.

4.3.1.7 Determination of unsaturation in latices containing particles whose surfaces have been functionalised with unsaturated units

Determination of the amount of the unreacted double bonds on the surface of polystyrene particles

functionalised with allylmethacrylate and isoprene units was carried out by the Wijs' method (11). Carbon-carbon double bonds in organic compounds can be determined by the quantitative addition of halogen to the double bonds. The halogen used may be bromine, iodine or iodine monochloride. The method described below (Wijs' method) uses iodine monochloride, and is the most common method used for the determination of unsaturation in polymers. Unsaturation is commonly expressed in terms of the so-called "iodine value", which is defined as the number of grams of iodine which has combined with one hundred grams of sample under the specified condtion.

The experimental procedure was as follows: An accurately weighed finely comminuted sample of the polymer (about 0.5g), obtained from the latex by drying, was dissolved in a mixture of chloroform (50ml) and o-dichlorobenzene (50ml) in a 250ml iodine flask fitted with a stopper, and warmed on a water bath. When the polymer had completely dissolved, the solution was cooled and 20ml of 0.2M of Wijs's solution (13g of iodine monochloride in 1000ml of acetic acid) was added quantitatively. The flask was placed in a dark cupboard for 30 minutes. At the end of this time, freshly-prepared potassium iodide solution (about 15ml of 50% solution) was added. The contents of the flask (which had now separated into two dark-red layers) was then titrated against 0.1M sodium thiosulphate solution with constant shaking until the aqueous layer was colourless. Freshly-prepared starch solution (5ml) was then added as an indicator, and the addition of sodium thiosulphate solution was continued until both layers remained colourless for one minute. Blank runs were carried out by titrating the solvents, potassium iodide solution and Wijs' solution against 0.1M sodium thiosulphate. The difference between the volume of 0.1M thiosulphate required for the sample titration and that required for the blank was used to calculate the iodine value.

4.3.1.8 Characterisation of polyacenaphthylene latex

The unique feature of the emusion polymerisation of acenaphthylene in this work was that the monomer remained as a crystalline solid throughout the emulsion polymerisation. For this reason, in order to confirm that a polymer has been produced, in addtion to total solids determination, the molecular weight of the polymer, the infrared spectra of the polymer in the form of a thin film and the electron micrographs of the polymer particles were obtained.

The total solids content was determined by coagulating the polymer latex in methanol, filtering the precipitated polymer through a Gooch crucible, and then drying in a vacuum oven at 50°C for 2 hours. The dried polymer was further extracted with methanol for 5 hours using Soxhlet extraction apparatus to ensure that all the unreacted monomer was eliminated. This procedure was used because the monomer is soluble in methanol.

The molecular weight of the polymer was determined by membrane osmometry for which a Mechrolab Model 501 (high-speed membrane osmometer) was used. Toluene was used as the solvent.

The infrared spectra of the polymer in the form of a thin film was obtained using a Perkin-Elmer Infrared Spectrophotometer. The polymer film was cast on a sodium chloride plate from a 30% toluene solution. The infrared spectrum is shown in Figure 4.2. The infrared spectrum of the monomer is shown for comparison.

The electron microscope was used to obtain information on the shape of the polymer particles as before. Figure 4.3 shows a typical electron micrograph of the polymer latex.

4.3.2 Characterisation of rubber latices

The total solids content, dry rubber content, mechanical stability (natural rubber only) of the rubber

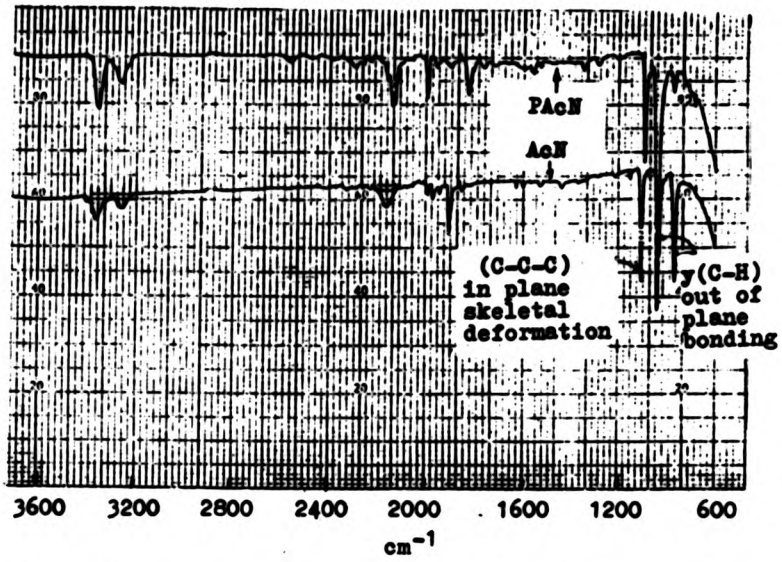


Fig. 4.2 Infra-red spectra of polyacenaphthylene and acenaphthylene

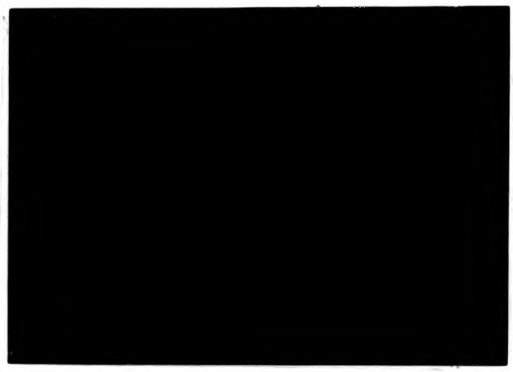


Fig. 4.3 Electron micrograph of polyacenaphthylene latex. Magnification X75,000

Table 4.9 Properties of rubber latices

	NR	SBR	NBR
Total solids content (%)	61.9	66.8	41.6
Polymer content (%)	60.0	65.5	41.6
Viscosity at 20°C (Brookfield, spindle No 4 at 30rpm) ($mNsm^{-2}$)	128	780	20.8
Surface tension at 20°C (mNm^{-1})	37.5	35.1	41.3
pH at 20°C	9.8	9.7	9.6
Mechanical stability (s)	800	-	-
Styrene content of contained polymer (%)	-	24	-
Acrylonitrile content of contained polymer (%)	-	-	32

latices were determined using the procedures specified in BS 1672 : 1972. The surface tensions were determined at 20°C using a Du Nouy surface tension apparatus. The pH and the viscosities were measured at 20°C using a Pye pH meter and Brookfield viscometer respectively. The properties of the rubber latices are given in Table 4.9.

4.3.3 Characterisation of blends of rubber and filler latices

4.3.3.1 Assessment of quality of filler dispersion by electron microscopy

It was assumed that latex blending would assure a uniform dispersion of the individual filler particles in the rubber matrix. However, replica electron micrographs were taken of the fracture surfaces of some of the rubber-filler mixtures as before in order to observe the actual state of dispersion. The state of dispersion was satisfactory.

4.3.3.2 Determination of viscosities of blends of rubber and filler latices

The viscosities of the blends were determined because of the anomalous viscosity changes which were observed on mixing the filler latices with natural rubber latex. A Haake-Rotovisko viscometer was used for the measurements, because it required only a small quantity of sample (40g). The Haake-Rotovisko is a rotational viscometer in which the sample is introduced into a circular gap between two coaxial concentric cylinders. One of these concentric cylinders is stationary, and the other rotates. The viscosity is determined from the resistance to rotation caused by the sample. The quantity actually measured is torque.

For these determinations, the natural rubber latex was diluted with distilled water to 26% total solids

content in order to obtain latex blends of moderate viscosity.

4.4 Compounding

In order to avoid possible complications which might have arisen from the use of sophisticated vulcanisation recipes, simple formulations consisting of the basic ingredients necessary to effect vulcanisation were used. The compounding formulation normally comprised rubber in the form of latex, polymeric filler in the form of latex, and a single dispersion of sulphur, zinc oxide, zinc diethyldithiocarbamate and antioxidant.

4.4.1 Preparation of aqueous dispersions of compounding ingredients

A single dispersion of the vulcanising ingredients was prepared. This dispersion contained all the vulcanising agents and the antioxidant in the ratios in which they were to be present in the latex compound. This practice was preferred, as the number of dispersions to be prepared and metered was reduced, and hence errors of compounding were minimised. The composition of the three types of dispersions prepared are given in Table 4.10. The dispersions were prepared by ball milling for 72 hours. The quality of each dispersion was checked using an optical microscope. The qualities were satisfactory.

4.4.2 Compounding of blends of rubber and filler latices

All the compounds were prepared by first blending the rubber and filler latices, and then adding the appropriate 50% dispersions of vulcanising agents of the composition shown in Table 4.10. The 50% dispersion refers to the total percentage of active ingredients (sulphur, zinc oxide, zinc diethyldithiocarbamate and antioxidant 2246). The blending was carried out in a 1000ml beaker by

Table 4.10 Recipes for prepering dispersions of vulcanising ingredients for rubber latex films

Ingredient	Parts by weight					
	NR		SBR		NBR	
	Dry	Actual	Dry	Actual	Dry	Actual
Sulphur	28.6	28.6	21.9	21.9	21.2	21.2
Zinodiethyldithiocarbamate	14.3	14.3	15.6	15.6	18.2	18.2
Zinc oxide	42.9	42.9	50.0	50.0	48.5	48.5
Antioxidant 2246 *	14.2	14.2	12.5	12.5	12.1	12.1
Water	-	37	-	37	-	37
Potassium hydroxide (10%)	0.2	2.0	0.2	2.0	0.2	2.0
Vulcastab LW (20%)	0.2	1.0	0.2	1.0	0.2	1.0
Dispersol LW (10%)	4.0	40	4.0	40	4.0	40
Methyl cellulose (1%)	0.2	20	0.2	20	0.2	20

* 2,2'-methylene bis(4-methyl 6-tertbutyl phenol)

Table 4.11 Compound formulations for latex films

Ingredient	Parts by weight					
	NR		SBR		NBR	
	Dry	Actual	Dry	Actual	Dry	Actual
Natural rubber latex (60% rubber)	100	167	-	-	-	-
Styrene-butadiene (24/76) rubber latex (66% total solids content)	-	-	100	152	-	-
Acrylonitrile-butadiene (32/68) rubber latex (40% total solids content)	-	-	-	-	100	250
Sulphur (50%)	2	4	1.75	3.5	1.75	3.5
Zincdiethyldithiocarbamate (50%)	1	2	1.25	2.5	1.5	3.0
Zinc oxide (50%)	3	6	4	8	4	8
Antioxidant 2246 (50%)	1	2	1	2	1	2
Potassium hydroxide (10%)	0.25	2.5	0.25	2.5	0.25	2.5
Polymeric filler latex	0-30	*	0-10	*	0-10	*

* as required according to total solids content of filler latex

stirring slowly (60rpm) for 10 minutes to avoid destabilisation. The latex blends were then allowed to stand for 24 hours in order to mature.

4.4.2.1 Blends of natural rubber and filler latices

The natural rubber latex was diluted as required (usualy to 26 and 45% TSC) before blending with the filler latices. The compound formulations are given in Table 4.11. Several difficulties were encountered when some of the filler latices, such as polystyrene and polyacenaphthylene latices, were added to the natural rubber latex. Problem of anomalous changes in viscosity and coagulation of an appreciable amount of the rubber were common. The coagulation appeared to be more severe as the concentration of the filler was increased and also when the blends were left to stand overnight. These problems were reduced by diluting the natural rubber latex (down to 26% TSC) and also by adjusting the pH of some of the latices to ca. pH 10.5. However, these problems were not encountered when filler latices containing rigid particles overcoated with a range of acrylate and methacrylate polymers were used. These problems are discussed more in detail in Section 5.14.

4.4.2.2 Blends of styrene-butadiene rubber and filler latices

The styrene-butadiene rubber latex was diluted to 50% total solids content before blending with the filler latices. The compound formulations are given in Table 4.11. No problems of anomalous changes in viscosity or coagulation were encountered when the filler latices were added to the rubber latex.

4.4.2.3 Blends of acrylonitrile-butadiene rubber and filler latices

The acrylonitrile-butadiene latex (50% TSC) was compounded as received without further dilution. The compound formulations are given in Table 4.11. No problems of anomalous changes in viscosity were observed on mixing the rubber latex with the filler latices. However, addition of the dispersion of vulcanising agents tend to destabilise the first sample of the rubber latex supplied by British Petroleum Company. This problem was not investigated further, as the second latex sample supplied the company was compounded without any problem.

4.4.3 Prevulcanisation of natural rubber latex and of blends of natural rubber and filler latices

A simple formulation containing only the ingredients necessary to effect prevulcanisation was used for preparing a single dispersion. In this way, it was hoped to avoid possible complications which might have arisen from the use of a sophisticated prevulcanisation recipe. The compound formulations are given in Table 4.12.

The apparatus used for the prevulcanisation was similar to that used for the preparation of the filler latices by emulsion polymerisation and shown in Figure 4.1. The natural rubber latex was diluted to 50% TSC. The diluted latex, stabiliser and potassium hydroxide were first weighed into the reaction flask. The flask and its contents were immersed in a thermostated water bath at 60°C. After equilibrium was attained (ca. 30 minutes), the required amount of dispersion of compounding ingredients was added and the prevulcanisation was carried out at 60°C for various periods of time ranging from 0.5 to 6 hours.

Further experiments were carried out by adding the filler latex to natural rubber latex before prevulcanisation. These experiments were carried out in order to see if adding the filler latex in this way would

Table 4.12 Compound formulations for filled and unfilled prevulcanised NR latex

Ingredient	Parts by weight			
	Unfilled		Filled	
	Dry	Actual	Dry	Actual
Natural rubber latex (60% rubber)	100	167	100	167
Sulphur (50%)	1	2	1	2
Zincdiethyldithiocarbamate (50%)	1	2	1	2
Zinc oxide (50%)	1	2	1	2
Antioxidant 2246 (50%) *	1	2	1	2
Water	-	33	-	167
Potassium hydroxide (10%)	0.5	5	0.5	5
Vulcastab LW (20%)	0.2	1	0.2	1
Polymeric filler latex	-	-	10	**

* 2',2'-methylene bis(4-methyl 6-tertbutyl phenol)
** as required according to total solids content of the filler latex

give better reinforcement than adding the filler latex to the natural rubber latex which was already prevulcanised. Following the same procedure outlined above, the filler latex was blended with the natural rubber latex and the latex blends were prevulcanised. The natural rubber latex was diluted as required (usually to 26 and 45% TSC depending upon the type of filler latex used) before mixing the filler latex with it.

4.4.4 Preparation of natural rubber vulcanisates containing polymeric filler particles and natural rubber vulcanisates containing carbon black

Experiments were carried out to compare natural rubber vulcanisates containing polymeric filler particles with natural rubber vulcanisates containing carbon black. In the case of the natural rubber-polymeric filler stocks, the blends of the filler and rubber latices were coagulated with dilute acetic acid, washed with deionised water and dried at 40°C for 24 hours. The vulcanising agents were not added at this stage. The vulcanising agents (Table 4.11) were added by mixing on a warm two-roll mill (50°C). Natural rubber gum and natural rubber containing super abrasion furnace black (SAF) were prepared by using an '00' Banbury internal mixer. The compounds were dumped at 95°C. The compound formulations and mixing procedures are given in Table 4.13.

4.4.5 Investigation of characteristics of unvulcanised mixes

A Monsanto rheometer, model 100, was used for assessing the cure characteristics of the various mixes, and the influence of the fillers upon the crosslinking process.

The testing procedures were as follows: The specimen (weighing about 10g) was placed in a rectangular cavity 50mm x 10mm. Embedded in the cavity is a biconical rotor

Table 4.13 Compound formulations and results for NR gumstock and NR containing carbon black

Ingredient	pphr	
	Gumstock	NR/CB45*
Natural rubber (SMR)	100	100
SAF black	-	45
Oil (Dutrex)	-	6.0
Sulphur	2.5	2.5
MBT **	1.0	1.0
Zinc oxide	4.0	4.0
Stearic acid	2.0	2.0
Nonox EXN	1.0	1.0
Dump temp. (^{o}C)	95	100
Mixing time (min.)	8	10
Density (Mgm^{-3})	0.97	1.11
Maximum torque	52	60
Minimum torque	14	12
Scorch time (min.)	2.88	4.13
Cure time at 90% crosslink (min.)	8.75	16.8

* NR/CB45 indicates that the material was an NR vulcanizate which contained 45pphr carbon black

** mercaptobenzthiazole - Anchor MBT

of diameter 37mm which is oscillated through an amplitude of 2° and 10° by means of a motor-driven eccentric. The cavity and specimen were maintained at a temperature of 100 0.5°C by electric heaters regulated by thermistor controllers, whilst the dies which form the cavity were held together by a force of about 1.5 MNm^{-2} exerted by means of a ram actuated by compressed air. On the the arm of the motor-driven eccentric are mounted strain gauges which measure the force required to oscillate the disc. The torque required to oscillate the disc was then plotted against time autographically while the sample was heated at the constant temperature (100°C).

4.5 Preparation of films from latices

4.5.1 Preparation of films from filled and unfilled natural rubber latex

Initially the films were cast on glass plate moulds, but this method was found to produce inhomogeneous films in the case of the latex blends, particularly with blends of natural rubber and polymethylmethacrylate latices. A dry-coagulant dipping method which gave satifactory films in all cases was therefore employed. The coagulant solution contained calcium chloride (10 parts), calcium nitrate (10 parts), cetyl trimethyl ammonium bromide (0.1 parts), industrial methylated spirit (65 parts) and water (14 parts) (all parts were by weight).

The dipping procedure was as follows: The formers (aluminium tubes) were thoroughly washed in detergent solution and then rinsed free of detergent with hot water. The formers were then further rinsed with softened water and then dried at 75°C. The hot formers were immersed in the coagulant solution, removed slowly and then dried at 75°C for 5 minutes. The formers (with their deposits) were allowed to cool at room temperature. The cool formers were then immersed in the latex for a period of time in the range 1 to 2 minutes, depending upon the viscosity of the

latex. The formers (with their latex deposits) were withdrawn slowly and rotated to even out irregularities.

The latex deposits were leached in water (45°C) for 2 minutes, dried at room temperature for 24 hours, and finally at 40°C for 1 hour. Films used for the determination of optimum cure were cured at 100°C for various periods of time ranging from 15 to 90 minutes. All other films were vulcanised at 100°C for 30 minutes (optimum cure time) (see Section 5.2).

4.5.2 Preparation of vulcanised moulded sheets from natural rubber containing carbon black and polymeric fillers

The natural rubber gumstock and natural rubber containing carbon black were vulcanised in a steam press at 150°C for 15 and 30 minutes in each case. These times and temperature were chosen because carbon black loaded natural rubber vulcanisates containing vulcanising agents in the ratios shown in Table 4.13 are generally (12) cured at temperature in the range 140 to 165°C for a period of time in the range 10 to 45 minutes, depending upon the end use of the vulcanisates. The compounded coagula containing polymeric fillers were vulcanised at 100°C for 30 minutes as for films obtained directly from the blends of the rubber and filler latices. A hydraulic pressure of ½ ton per sq. inch of mould area section was used in all cases.

4.5.3 Preparation of films from filled and unfilled styrene-butadiene rubber latex

The films could not be prepared satisfactorily by dipping, because wet-gel strengths of the latex deposits were too low. The latex films were therefore prepared by casting on a glass plate moulds as described in BS 1672 : 1972. The cast films were left to dry at room temperature (ca. 20°C) for 24 hours, then stripped off the mould and dried at 40°C for 1 hour. Films used for the

determination of optimum cure were cured for various periods of time ranging from 15 to 120 minutes. All other films were vulcanised at 100°C for 45 minutes (optimum cure time).

4.5.4 Preparation of films from filled and unfilled acrylonitrile-butadiene rubber latex

The films were prepared by coagulant dipping in the same way as films from natural rubber latex were prepared (Section 4.5.1). They were also vulcanised at 100°C for 45 minutes as for films from styrene-butadiene rubber latex.

4.6 Measurement of mechanical properties of films

The limits of reliability of the mean of the various properties determined were evaluated using the method outlined in Appendix B.

4.6.1 Tensile stress-strain properties

The stress-strain measurements were made using an Instron testing machine (model 1026). The machine was used in conjuction with the Instron optical extensometer by means of which a continuous indication of the load and elongation on the test-piece was recorded autographically. Dumbell (type D) test-pieces were die-cut from films of the vulcanisate using an ISO tensile test-piece cutter. The test-pieces were pre-conditioned by stretching to about 10% three times and then allowed to recover for 30 minutes before testing. The ultimate tensile properties were determined essentially by the method described in BS 903 : 1971. A minimum of 10 test-pieces were tested from each stock. The tensile stress at break was calculated by dividing the load at break by the initial cross sectional area of the test-piece. The tensile modulus at 300% extension was calculated by dividing the load at this elongation by the initial cross sectional area of the

test-piece. The values of these properties were found to be independent of the direction at which the test-pieces were cut (i.e., the films did not show significant anisotropy).

4.6.2 Measurement of stress relaxation

Measurements of stress relaxation were carried out using a Wallace-Shawbury stress relaxometer with test-piece extended to 100% extension. Test-pieces in the form of 0.4cm x 4.0cm strips were cut from the films. The decay in stress was autographically recorded up to a period of 24 hours. From the chart, the stresses at zero time and at various times were calculated. The fractional stress retained was then plotted against time.

4.6.3 Measurement of tear force

Crescent test-pieces with a nick of depth 1 ± 0.2mm at the centre of the inner edge of the test-piece were used (BS 903 : Part A3 1982). The test-piece was gripped and stretched (at 500 mm/min) to break in an Instron testing machine. The maximum force reached was recorded. The tear strength was calculated by dividing the maximum force by the thickness of the test-piece. A minimum of 10 test-pieces were tested from each stock.

4.6.4 Measurement of puncture force

Puncture force was measured using a procedure (13) in which the force required to cause a ball-point pen to puncture the latex film was determined. The unstretched latex film was clamped by a ring and mounted in the Instron testing machine (model 1026). The indentor was a pilot Hi-Tec point pen. It was mounted in the crosshead as shown in Figures 4.4 - 4.8. The force required to cause penetration of the film was measured at a cross-head speed of 10 mm/min. The puncture strength was calculated by

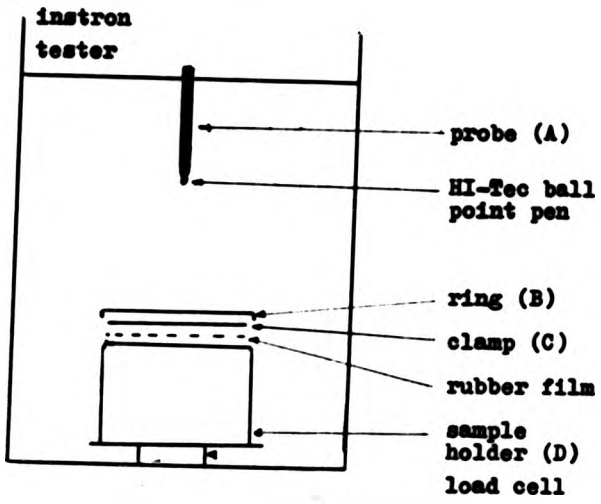


Fig. 4.4 Experimental arrangement for the determination of puncture strength

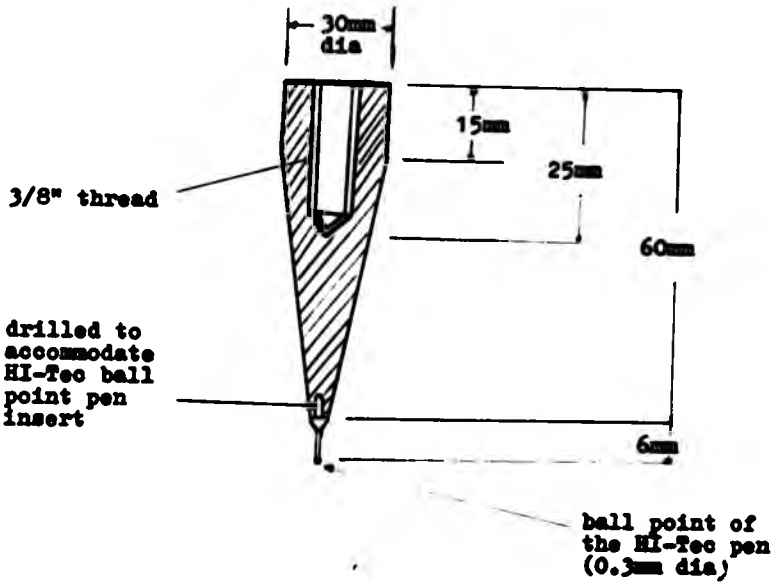


Fig. 4.5 Dimensions of probe A in Fig. 4.4

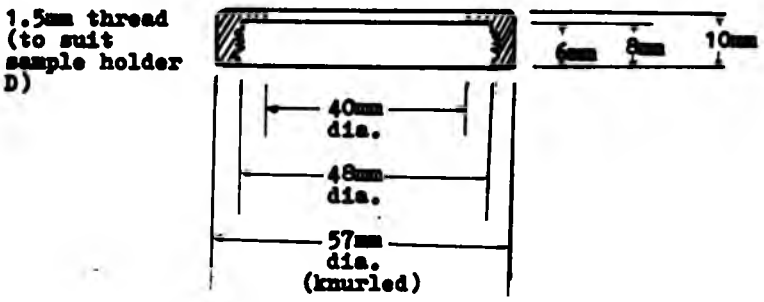


Fig. 4.6 Dimensions of clamp B in Fig. 4.4

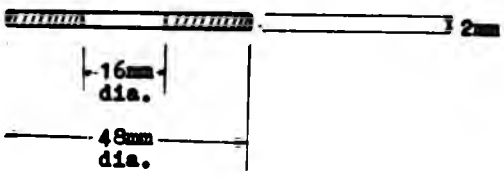


Fig. 4.7 Dimensions of ring C in Fig. 4.4

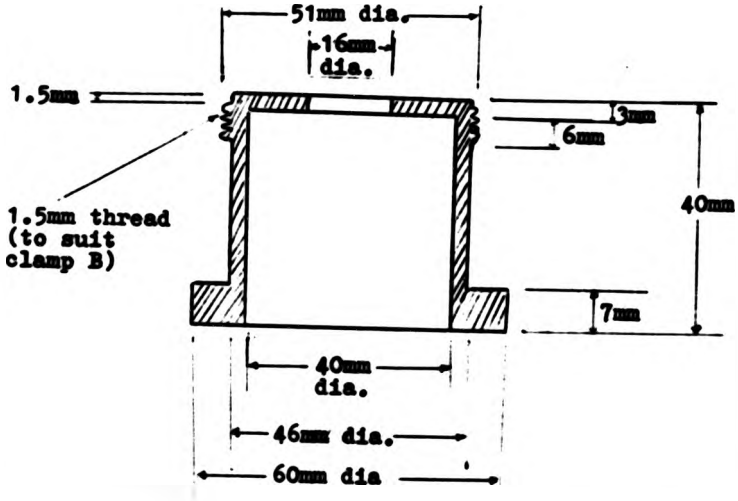


Fig. 4.8 Dimensions of sample holder D in Fig. 4.4

dividing the maximum force recorded by the thickness of the latex film. A minimum of 12 films were tested from each stock. This techinque was found to give reproducible results.

4.7 Further examination of latex films

4.7.1 Examination of broken tensile test-pieces by scanning electron microscope

The ruptured surfaces of the used tensile test-pieces were examined by scanning electron microscope in order to gain some indication of the adhesion between the polymeric fillers and the rubber matrix. The ruptured surfaces were coated with gold prior to examination.

4.7.2 Determination of extractability of filler

The extractability of the filler was determined using Soxhlet extraction apparatus with toluene at 80°C. 0.5g samples were used, and extraction was continued for several days. At the end of the selected extraction period, the extracted sample was dried to constant weight in a vacuum oven at 50°C. The percentage weight of filler extracted was then calculated from the percentage weight loss. These data were then used to estimate the extent of chemical bonding between the filler particles and rubber matrix in which they were embedded. It was expected that a low percentage of filler extracted would indicate existence of chemical bonds between the filler and rubber matrix. It should be noted that the filler particles were themselves completely soluble in toluene under the condition stated above.

CHAPTER FIVE : RESULTS AND DISCUSSION OF MECHANICAL REINFORCEMENT OF POST-VULCANISED NR LATEX FILMS BY POLYMER PARTICLES

5.1 Introduction

The results of this investigation of the mechanical reinforcement of post-vulcanised NR latex films are presented and discussed in this chapter. The statistical significance of some of the results were tested using the t-test and the Wilcoxon test (1). The latter statistical test is a non-parametric test which utilises information about the relative magnitude and the direction of the difference within two sets of results. In addition to the various graphs presented, the significances of the results obtained in the present investigation have been assessed on the basis of these statistical tests. Programs for the t-test are shown in Appendices C1 and C2.

Throughout the presentation and discussion of the results, the polymeric filler particles and the methods used for their preparation are designated as before, but for convenience the significance of the codes is restated in some cases.

5.2 Determination of optimum cure of films from filled and unfilled NR latex

In order to estimate the optimum cure for the films from NR latex containing the various polymeric filler particles used in the investigation, NR latex films containing PS and PMMA of particle sizes 68nm and 69nm respectively were vulcanised at 100°C for various periods of time, ranging from 15 to 90 minutes. These two polymeric fillers were chosen mainly because they are the obvious cheap rigid polymers to use, and therefore the obvious starting point. It also afforded an oppportunity to investigate the effect of cure time upon the ability of

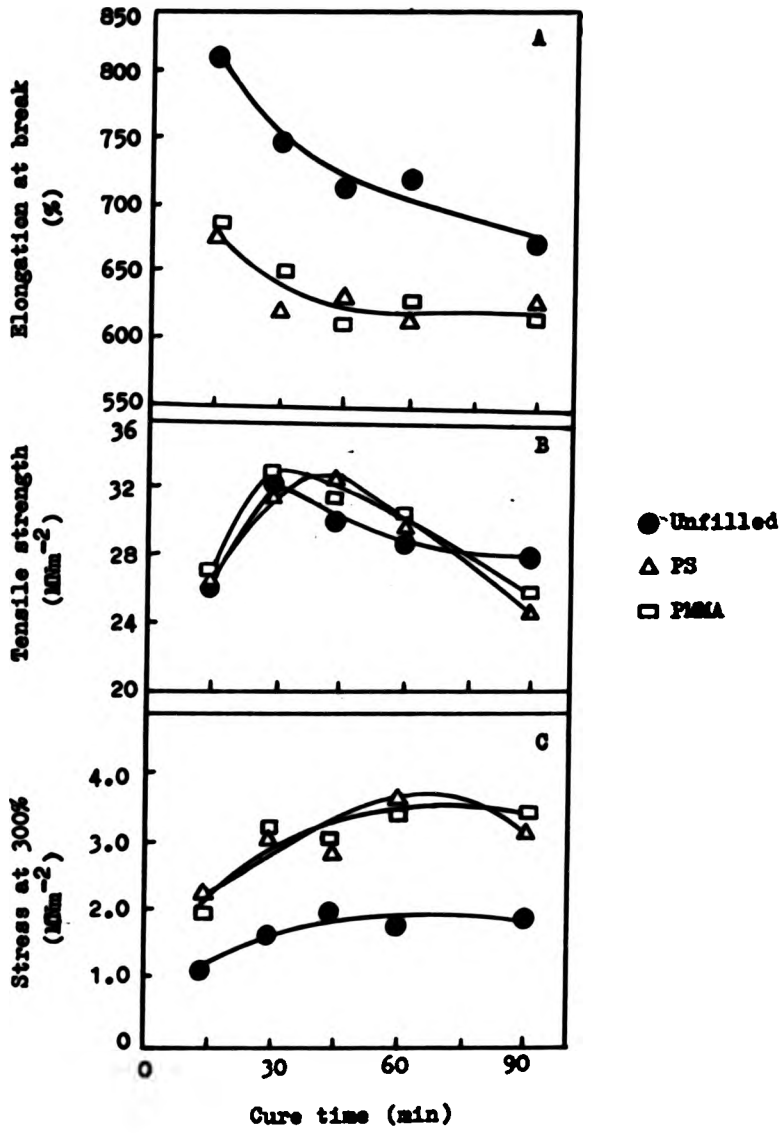


Fig. 5.1 Effect of cure time at 100°C upon mechanical properties of films from filled and unfilled NR latex. Filler loading: 10 pphr; particle sizes: PS - 68nm, PMMA - 69nm

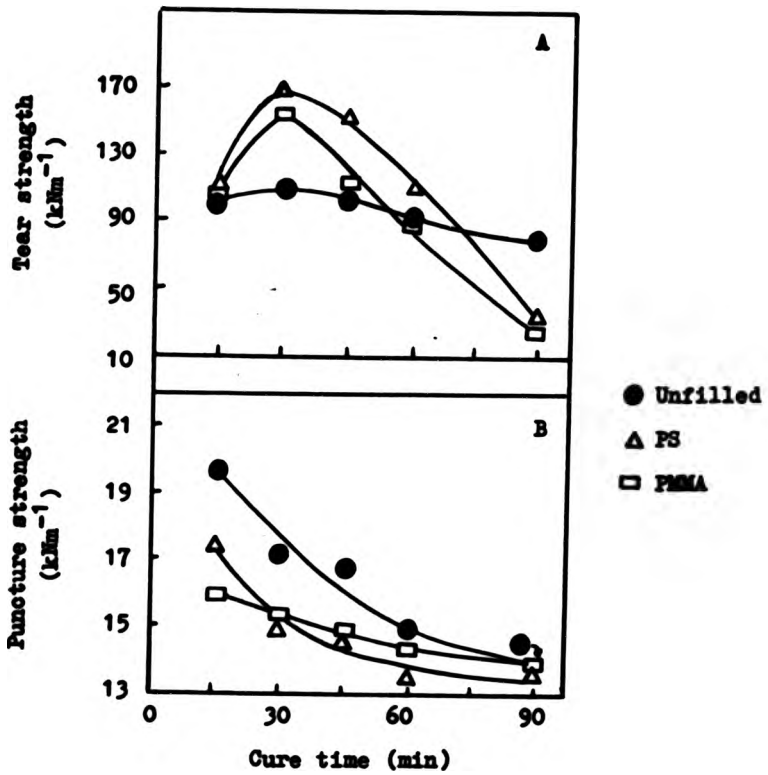


Fig. 5.2 Effect of cure time at 100°C upon mechanical properties of films from filled and unfilled NR latex. Filler loading: 10 pphr; particle sizes: PS - 68nm, PMMA - 69nm

rigid polymer particles of the same T_g but different polarities, to reinforce.

Figures 5.1 and 5.2 show the effect of cure time upon the mechanical properties of filled and unfilled latex films. It can be seen that the various properties reached their maximum values at different cure times. The tensile strengths of all the film vulcanisates decreased rapidly on prolonged cure, but not all decreased at the same rate: the decrease of tensile strength of the unfilled films was less rapid than that for the filled films. The stress at 300% extension increased, the rate of increase becoming less rapid with increasing cure time. The elongation at break and puncture strength decreased with increasing cure time, while the tear strength reached an optimum value at about 30 minutes cure. Of particular interest is the effect of prolonged cure upon the tear strength of the filled films giving very low tear strengths after 90 minutes cure. Since the enhancement of tear strength and puncture strength were taken as the primary criteria of reinforcement, rather than enhancement of tensile strength and modulus, an optimum cure of 30 minutes at 100°C was selected. Unless otherwise indicated, all the films obtained from NR latex containing the various polymeric filler particles were cured for 30 minutes at 100°C.

A possible reason for the reduction of the strength properties of films containing PS and PMMA on prolonged cure is deformation of the spherical rigid filler particles on prolonged cure. One would expect the rigid particles to be softened on prolonged cure, because the cure temperature is very close to the T_g of these polymeric fillers. Evidence for this explanation comes from a comparison of scanning electron micrographs of NR latex films filled with PS particles and cured at 100°C for 30 minutes and 90 minutes. Figure 5.3A shows a typical fractured suface of a film cured for 30 minutes. It can be seen that the filler particles retained their spherical nature. Figure 5.3B shows a typical fractured surface of a film cured for 90 minutes. Here, the individual filler

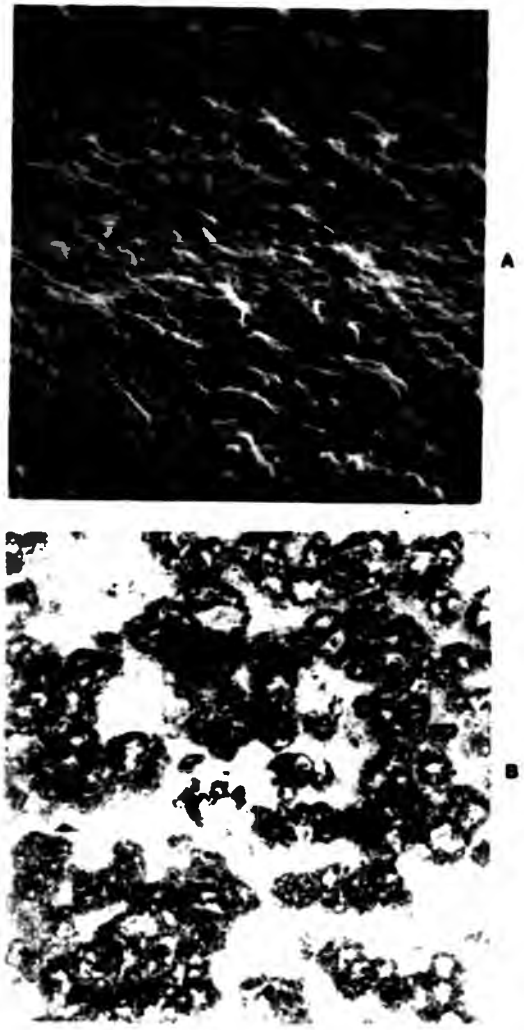


Fig. 5.3 Scanning electron micrographs of fractured surfaces of tensile test-pieces of films from NR latex containing 10 pphr of PS particles: (A) sample cured for 30 minutes; (B) sample cured for 90 minutes; magnification X 5,000

particles appear to have lost their spherical nature.

5.3 Results of cure characteristics of films from filled and unfilled NR latex

The cure characteristics of the films obtained from filled and unfilled NR latex containing the various polymeric filler particles were assessed using a Monsanto rheometer, as described in Section 4.4.5. From the time-torque (stiffness) curves (see Fig. 5.4 for typical curves) obtained, the following characteristics were derived :

I) minimum torque : this is indicative of the viscosity of the unvulcanised film at the vulcanising temperature;

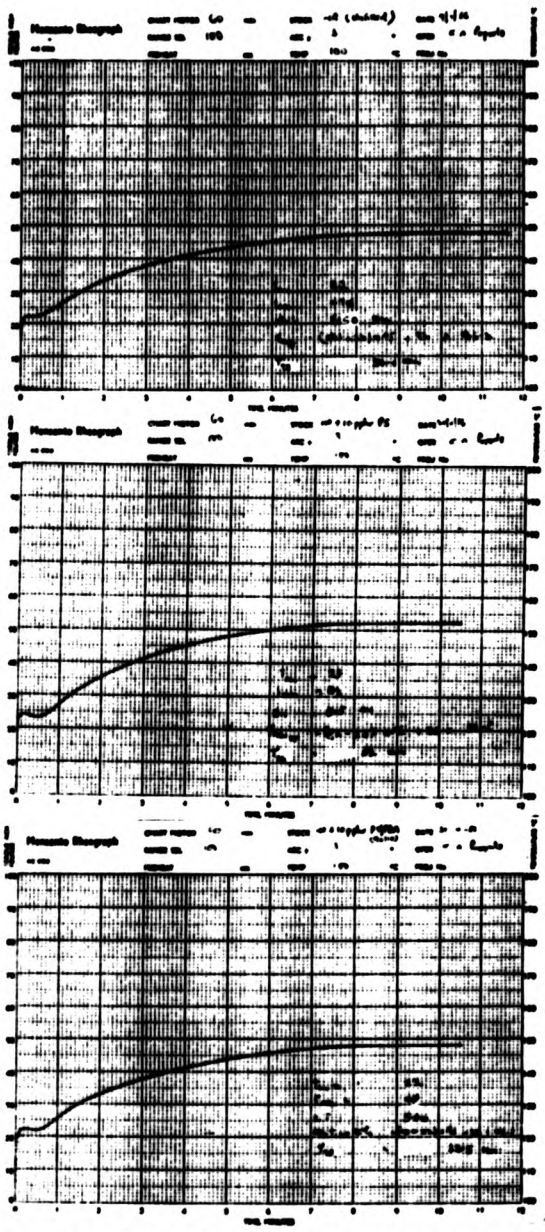
II) induction time (or scorch time) : this is the time required for a fixed small rise above the minimum torque;

III) maximum torque : this is indicative of the elastic modulus of the fully-vulcanised film at the vulcanisation temperature;

IV) time to 95% of the maximum torque, T_{95} : this is approximately equivalent to a technical cure (or optimum cure);

V) extent of crosslinking : this is indicated by the difference between the maximum and minimum torque values.

Table 5.1 gives results for the cure characteristics of selected filled films. Table 5.2 gives results for the effect of filler (PS) loading upon the cure characteristics. It can be seen from Table 5.1 that the values of T_{95} for all the filled films are more or less the same with the exception of the films containing PAcM. These results justified the conclusion drawn from the results presented in Section 5.2 that an optimum cure of 30 minutes, obtained for vulcanisates containing PS and



(A)

(B)

(C)

Fig. 5.4 Typical rheometer traces of unfilled NR latex films (A) and NR latex films containing 10 pphr of (B) PS (69nm) and (C) PS/PBA (90/10) core-shell (74nm); magnification X 5,000

Table 5.1 Cure characteristics of films from NR latex containing various filler particles

Filler 10pphr	Induction time min	t_{95} min	Minimum torque lbin	Maximum torque lbin	Extent of cross-linking lbin
None	5.50	34.0	22.0	47.5	25.0
PBA	5.50	34.5	19.0	40.5	21.5
PS	5.50	32.0	23.0	52.0	29.0
PAcN	6.50	41.0	24.5	58.5	34.0
Crosslinked PS	5.25	30.0	24.0	56.0	32.0
PS/PBA (90/10)	5.20	33.5	22.0	48.0	26.0
PS/PBA (80/20)	5.25	32.0	22.0	47.0	25.0
PS/PBA (50/50)	5.00	31.5	21.0	48.5	27.5

Table 5.2 Typical effects of filler (PS) loading upon cure characteristics of films from NR latex

Filler level pphr	Induction time min	t_{95} min	Minimum torque lbin	Maximum torque lbin	Extent of cross-linking lbin
None	5.50	34.0	22.0	47.5	25.0
5	4.50	27.5	20.5	49.0	28.5
10	5.50	32.0	22.0	52.0	30.0
20	5.50	37.0	24.0	61.0	37.0
30	6.00	41.0	25.5	65.0	39.5

PMMA particles, could be used for NR vulcanisates containing all other types of polymer particle used in this investigation.

Table 5.2 shows that cure time (and induction time) appears to go through a minimum and then increase as filler loading is increased. Similar effects have been observed in NR vulcanisates containing carbon black (2). However, these effects were not further investigated in the present work, because optimum reinforcement as judged by enhancement of tear strength, was attainable at 10-20 pphr filler loadings. 10 pphr was the preferred loading, because the moduli obtained for film vulcanisates containing this loading were lower than for film vulcanisates containing higher loadings of fillers. Also the rubber-filler latex blends appeared to give more homogeneous films at 10 pphr loading than at higher loading, as stated in Section 4.4.2.1.

5.4 Results of assessment of quality of filler dispersion by electron microscopy

As remarked in Section 4.3.3.1, it was assumed that the blending of the rubber and filler in the form of latex would ensure uniform dispersion of the individual filler particles in the dried rubber films. In order to investigate this matter further, replica electron micrographs were taken of the fracture surfaces of the various vulcanised filled films so that the actual state of dispersion could be observed. A selection of the electron micrographs obtained are shown in Figure 5.5. Although the resolution achieved by the electron microscope is not as effective as was desired, and also the pictures are noisy (due to an electronic fault in the instrument), the dispersion appears generally good and individual particles can be recognised.

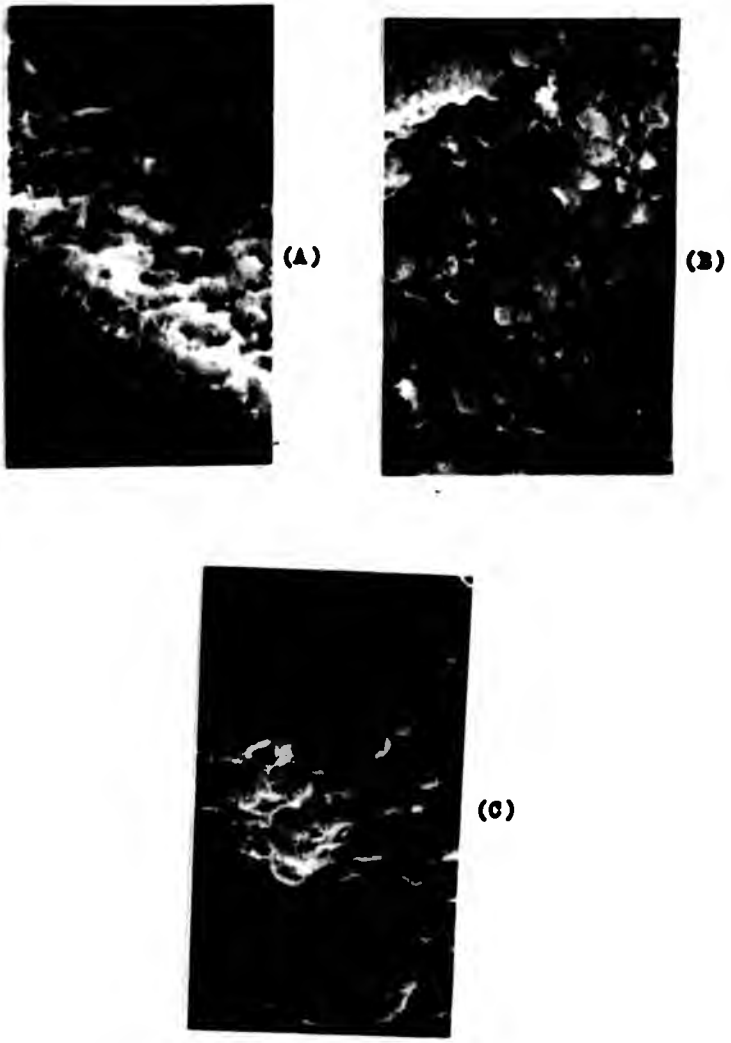


Fig. 5.5 Scanning electron micrographs of fractured surfaces of NR film vulcanisates containing 10 pphr of various fillers: (A) PMMA (69nm); (B) PS (68nm); (C) PS/PBA (80/20) core-shell (69nm); magnification X 5,000

5.5 Effect of size of filler particle

The effects of the size of the filler particles upon mechanical properties are shown in Figures 5.6 and 5.7. These figures show the variation of various mechanical properties of vulcanised films with particle size for NR film vulcanisates containing 10 pphr of PS and PMMA. The particle diameters were 45nm, 68nm, 265nm, 455nm for PS, and 50nm, 69nm, 250nm, 480nm for PMMA. All the filler latex particles were essentially monodispersed with the exception of the particles of average sizes 45nm (for PS) and 50nm (for PMMA). These latex particles had polydispersity indices (see Section 4.3.1.1 for definition) of 4 and 6 respectively. The properties of the vulcanisates containing the polydispersed particles are represented by the filled rectangular and triangular points in the various plots. Because the mechanical properties of the films containing the polydispesed particles were not reproducible, the values indicated by the filled points are not regarded as being accurate. It can be seen from the various plots that elongation at break and puncture strength increased, whilst tear strength, tensile strength and stress at 300% extension decreased with increasing particle size of filler. The various mechanical properties of the filled films vary approximately linearly with the filler particle diameter.

From these results, it is evident that small particle size is a necessary prerequisite for the manifestation of reinforcement in the system under investigation, as judged by enhancement of tear strength and tensile strength. However, the reason for the effect of filler particle size upon reinforcement is not entirely clear. The increase of strength properties with decreasing filler particle size observed in this work can be attributed to the increase in interfacial area per unit volume of filler as particle size decreased. It can also be attributed to stress concentration brought about by small filler particles. Also the distance between

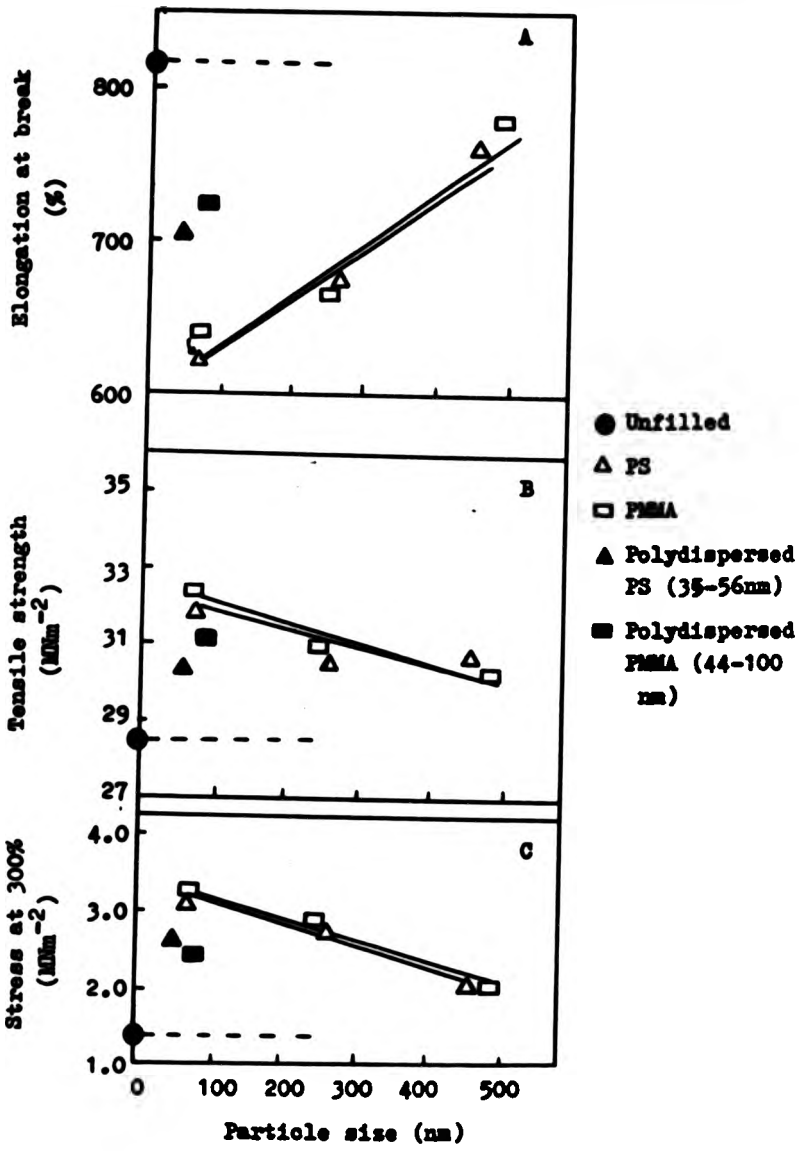


Fig. 5.6 Effect of particle size of filler upon mechanical properties of NR film vulcanisates. Filler loading: 10 pphr

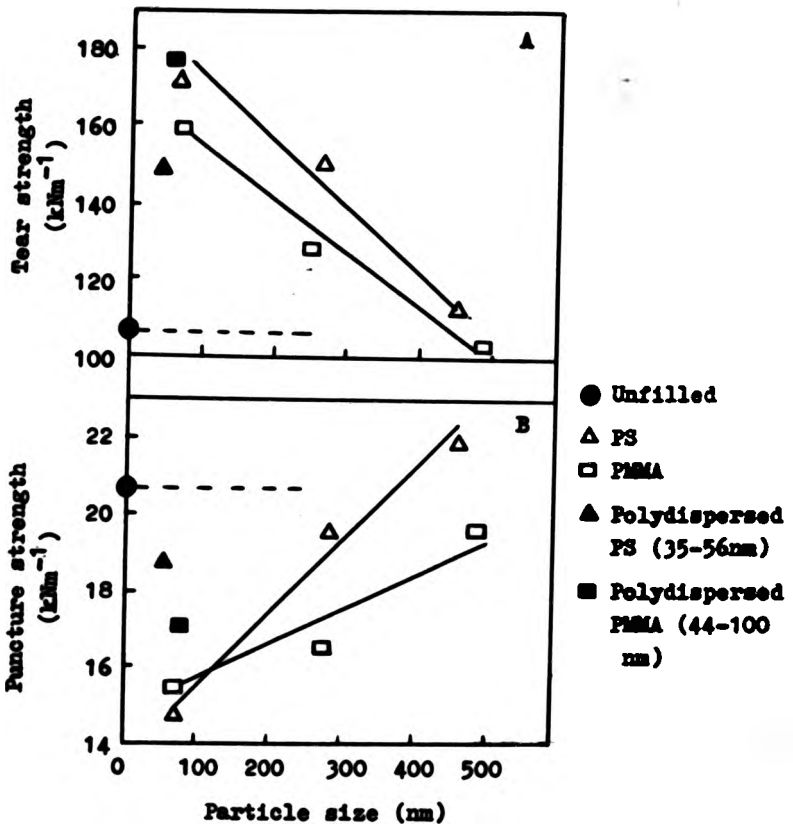


Fig. 5.7 Effect of particle size of filler upon mechanical properties of NR film vulcanisates. Filler loading: 10 pphr

neighbouring particles decreases with decreasing particle size. For instance, for the latex films containing 10 pphr of PS particles of diameter 68nm, 265nm and 455nm, the average distances between the neighbouring particles are 75nm, 291nm and 500nm respectively. As the particle size decreases, the surface area of a given aggregate volume of particles increases, and the tendency of particles to agglomerate increases with a corresponding decrease in the maximum packing volume. This effect will be expected to increase tensile stress. The distribution of particle sizes must also be an important factor. Mixtures of different particle sizes can pack more densely than monodipersed particles. Thus, a distribution of particle sizes should give a larger maximum packing fraction, and therefore lower tensile stress for a given concentration (see equation 2.6 Section 2.2). This effect is evident from the tensile stress at 300% extension observed in the present work for films containing polydispersed particles shown in Figure 5.6C. Sweeny and Geckler (3) have argued that, for bimodal mixtures, if the particles differ in diameter by a ratio of about 7 to 1, the small particles can thread their ways through the passages between the larger particles so that very efficient packing can occur. This effect, as remarked before, decreases tensile stress. The probable reasons for the manifestation of reinforcement by small particles discussed above may well account for the discrepancy between theory of the enhancement of tensile modulus and experimental results obtained by various workers, as already discussed in Chapter two (Section 2.1.2).

5.6 Effect of rigidity of filler particle

PS, PMMA and PAcN of particle sizes 68nm, 69nm and 90nm respectively were used in order to study the effect of the rigidity of the filler particles upon extent of reinforcement of films from NR latex. PBA of particle size 76nm was also used in order to investigate the effect of a

synthetic polymer having T_g (-57°C) close to that of NR (-70°C). Blends of NR latex and PAcN latex containing more than 5 pphr of the latter were found to contain micro coagulum on standing for few hours. This problem was overcome by adding a large quantity of potassium hydroxide (10-20 parts by weight per hundred parts of filler in the blend). The likely effect of potassium hydroxide contained in the blend will be discussed later in this section. However, no problem was experienced with the blend containing 5 pphr of the filler. The effects of the various fillers upon the mechanical properties of films obtained from NR latex are given in Table 5.3. Figure 5.8 shows tensile-stress strain curves for the unfilled film and for films containing 10 pphr of the various fillers. Thus, it appears that the T_g of the filler particle affects the way it reinforces the film, and also that the reinforcing abilities of these fillers are directly related to the magnitude of the rigidity.

The reinforcement of films from NR latex by these fillers can best be compared at the 5 pphr filler loading, since homogeneous films were obtained for all the various blends of the rubber and filler latices at this loading. The stress at 300% extension and tear strength appear to increase with the rigidity of the filler particles, whilst the elongation at break decreases. No direct relationship between the tensile strength of the film vulcanisates and the rigidity of the contained particles was obtained. This is also the case for puncture strength. The very low tear strengths of the film vulcanisates containing 10 pphr and 15 pphr of PAcN particles, as given in Table 5.3, is presumably a consequence of the large amount of potassium hydroxide which was required to stabilise the rubber latex containing the filler particles, as described above. In this case, the tear proceeded steadily and produced smooth torn surfaces. This is in contrast to what was observed at the same loadings for the films containing PS and PMMA particles, the tearing of which proceeded in a "knotty" manner to leave rough irregular torn surfaces. Hence, PS

Table 5.3 Mechanical properties of NR film vulcanisates containing various polymeric filler particles of different rigidities

Filler	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}	Nature of tear
pphr						
None	28.7	833	1.34	106	19.5	N
5-PBA	27.5	800	1.45	104	18.0	N
5-PMMA	31.9	788	2.15	118	17.6	N
5-PS	32.0	740	2.20	122	18.3	N
5-PAcN	30.0	720	2.39	136	18.5	K
10-PBA	24.9	787	1.66	108	15.9	N
10-PMMA	30.6	745	2.85	165	16.0	K
10-PS	30.5	715	2.91	162	15.5	K
10-PAcN	22.4	663	3.16	47.8	19.8	N
15-PMMA	29.5	704	3.80	160	15.2	K
15-PS	28.5	668	3.66	165	16.0	K
15-PAcN	20.8	583	4.18	50.6	18.5	N

Particle sizes: PBA - 80nm, PMMA - 69nm, PS - 68nm, PAcN - 90nm

K - knotty
N - not knotty

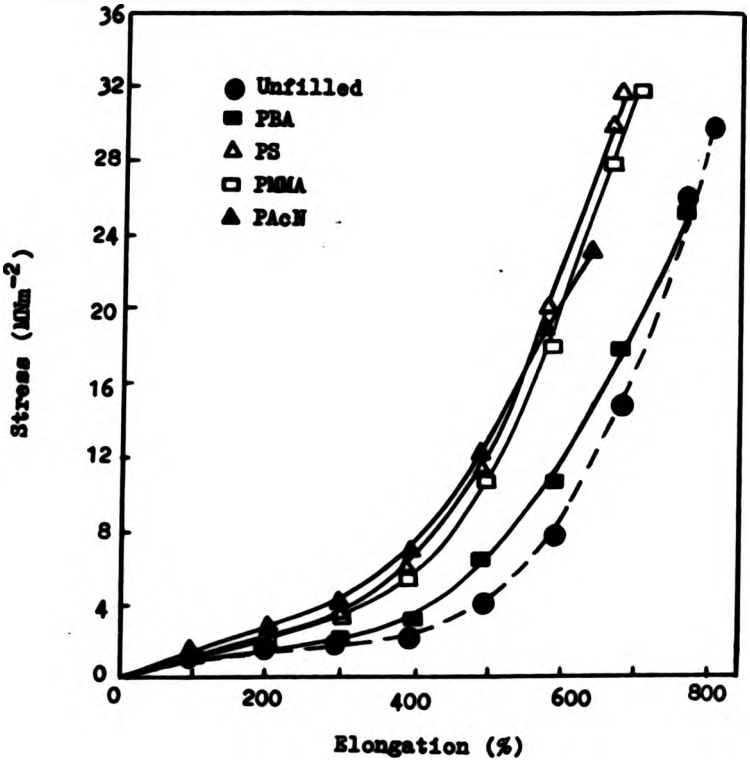


Fig. 5.8 Effect of rigidity of filler particles upon tensile stress-strain curve for NR film vulcanisates containing various fillers. Filler loading: 10 pphr. Particle sizes: PBA - 76nm, PS - 68nm, PMMA - 69nm, PAcN - 90nm

and PMMA particles gave higher tear strengths than did PAcN particles at 10-15 pphr loadings. Table 5.3 and Figure 5.8 show that there is no signicant difference in the reinforcing ability of PS and PMMA particles, indicating that the polarity of the polymer does not have a significant effect upon the reinforcement of post-vulcanised films from NR latex by polymeric filler particles. The knotty character of the tearing of the film vulcanisates containing PS and PMMA particles was more pronounced at 10-20 pphr filler loadings than at 5 pphr loading.

Previous studies by Morton *et al.* (4,5) in which polymeric fillers, such as PS, PMMA and PAcN particles, were used for reinforcing NR and SBR, have shown that the tensile strengths of the filled vulcanisates depended upon the magnitude of the modulus of the contained filler (Section 2.1.4), increasing with increasing filler modulus. As stated in Chapter Two (Section 2.1.4), these workers prepared their vulcanised sheets from the coagulum of the blends of the rubber and filler latices rather than directly from the latex blends as was the case in the present investigation. The dependence of the tensile strengths of the filled rubber vulcanisates upon the rigidity of the contained filler particles observed by these workers is contrary to the findings in the present investigation. As remarked before, no direct relationship was found between the tensile strengths of the film vulcanisates and the rigidity of the contained polymer particles. This difference could probably be due to the way Morton *et al.* prepared their vulcanisates. No measurements of tear strength and puncture strength were reported by these workers. The tear strength of the unfilled NR may well have been lower in their case, because they masticated the rubber.

The effects of the PS and PMMA particles upon stress relaxation behaviour of the film vulcanisates are shown in Figure 5.9. Attempts were made to derive relaxation-time spectra from these curves. The stress relaxation behaviour

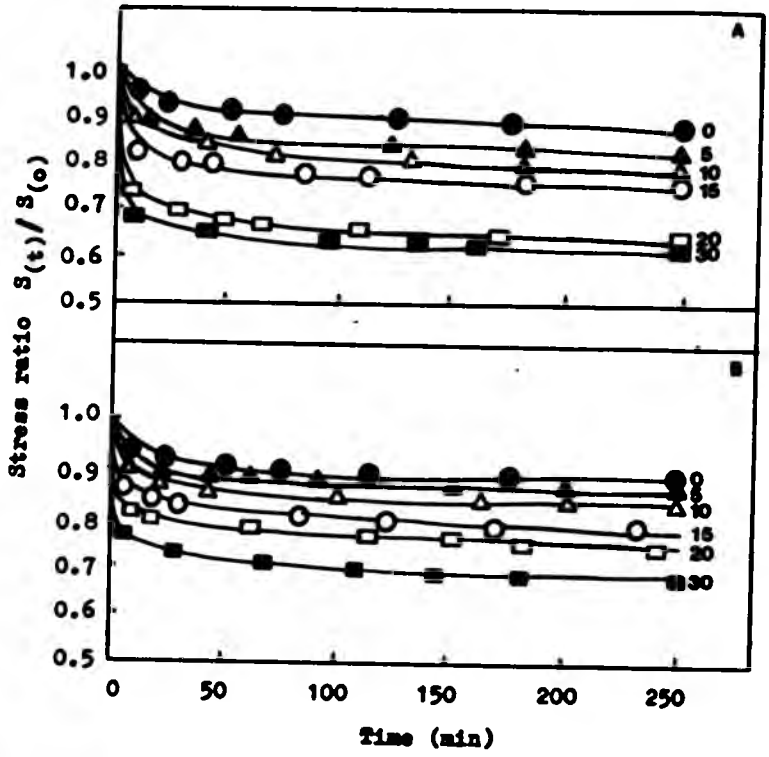


Fig. 5.9 Effect of PS (A) and PMMA (B) particles upon stress relaxation of NR film vulcanisates. Figures appended to curves indicate the filler loading in pphr. Particle sizes: PS - 68nm, PMMA - 69nm

of the film vulcanisates indicates that the presence of the rigid particles in the rubber matrix creates hydrodynamic disturbance which is accompanied by lengthening of the relaxation-time spectrum of the film vulcanisates. Payne (6) has provided evidence to support this hypothesis. Thus, in a similar fashion, the presence of carbon black in filled vulcanisates will extend the time spectrum at long times and at high temperature by many decades.

5.7 Effect of crosslinking of filler particles

The effects of crosslinking of PS particles and PMMA particles upon their abilities to reinforce films obtained from NR latex are given in Table 5.4. Crosslinking these filler particles appears not to affect the enhancement of tear strength significantly. However, the puncture strength showed a slight improvement. The elongation at break decreased and tensile stress at 300% extension increased with the degree of crosslinking, the degree of crosslinking being indicated by the level of crosslinking agent and the swelling of the crosslinked particles in toluene. The tensile strength appears to decrease with the degree of crosslinking. The major problem encountered with these crosslinked particles was that the rubber latex containing these particles did not produce such good films as did the rubber latex which contained uncrosslinked particles. This may well account for the inability of these particles to give enhanced tear strength.

The most significant effect of crosslinking the filler particles was that the films derived from the rubber latex containing the particles appeared to be "leathery" in texture, unlike the films obtained from the NR latex which contained uncrosslinked particles.

Table 5.4 Effect of crosslinking of PS and PMMA particles upon reinforcement of NR film vulcanisates

Filler	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}	Nature of tear
pphr						
None	28.7	833	1.34	106	19.5	N
10-PS (not XL)	30.5	715	2.91	162	15.5	K
10-PS (XL 0.5)	31.0	725	2.78	160	22.7	K
20-PS (XL 0.5)	28.4	658	3.16	170	16.6	K
10-PS (XL 2.0)	29.1	644	3.09	160	21.1	K
10-PS (XL 5.0)	28.0	630	3.00	137	18.0	K
10-PMMA (not XL)	30.6	745	2.85	165	16.0	K
10-PMMA (XL 0.5)	30.0	750	2.82	167	24.0	K
20-PMMA (XL 0.5)	23.5	635	2.97	170	17.0	K
10-PMMA (XL 2.0)	27.0	622	3.15	156	22.7	K
10-PMMA (XL 5.0)	26.0	615	3.20	152	17.5	K

XL 0.5: XL indicates crosslinked particles. The number indicates the parts by weight of the crosslinking agent per 100 parts by weight of monomer

Particle sizes: PS - 68nm, PMMA - 69nm, crosslinked PS - 72nm, crosslinked PMMA - 73nm

5.8 Effect of reducing glass- transition temperature of polymeric filler particles by copolymerising with butylacrylate

It is clear from the results discussed above that PS and PMMA filler particles of small sizes conferred enhanced tear strength, and that crosslinking the filler particles has no significant effect upon their abilities to reinforce.

The results of a broad survey of the effects of copolymerising the "rigid" monomer of the polymeric filler with a "plasticising" monomer in various ways are presented in the present section. In this part of the investigation, the effect of reducing the T_g of PS by copolymerising with butylacrylate, and the effect of particle morphology (random, core-shell, etc.) of styrene/butylacrylate copolymer particles, keeping overall compostion constant were investigated.

5.8.1 Characterisation of styrene/butylacrylate copolymer latices

Copolymers of styrene and butylacrylate were prepared in various ways, as outlined in Section 4.2.4. The particle sizes and surface tensions of the various copolymer latices showed (Table 4.7 Section 4.2.4) that copolymers prepared by the seeded-growth method (indicated by SE) and shot-growth method (indicated by SH) give particles which probably have a core-shell structure consisting of an inner core which is rich in polystyrene and an outer shell which is rich in polybutylacrylate. In the case of the conventional method (indicated by CON), a latex whose particles contain uniform copolymer of stryrene and butylacrylate was formed as expected. It was expected that if the rigid PS particles (core) are completely overcoated with PBA (shell), the surface tension of the latex containing the core-shell particles would be similar to that of PBA latex rather than that of

PS latex, it having been found that PS and PBA latices have significantly different surface tensions (58.0 mNm^{-1} and 43.8 mNm^{-1}) in the present work. The nature of the particle shell should also be reflected in the observed viscosity changes which occur when core-shell polymer latices are blended with NR latex. Both the surface tensions and the observed viscosity changes are consistent with the particle shell being rich in PBA (see Section 5.14).

As remarked in the experimental Section (4.2.4b), it was not possible to prepare particles having a core-shell particles which comprise a soft core rich in polybutylacrylate and a rigid outer shell rich in polystyrene, because of the occurrence of phase inversion. Thus, the styrene monomer added to the polybutylacrylate seed latex presumably enters the particles, polymerises, phase separates and forms polystyrene domains within the soft polybutylacrylate particles, rather than forming an external hard polystyrene shell (7,8). The characteristics of these copolymer latices (indicated by INV) showed that they are similar both to those prepared by seeded-growth and to those prepared by shot-growth methods.

For the core-shell polymer latices prepared by the shot-growth method, the coat would be expected to be more strongly bound to the core particles than is the case for core-shell particles produced by seeded-growth. Some evidence in support of this expectation is provided by a comparison of scanning electron micrographs of films cast from the core-shell latices. The films were not all that coherent. Figure 5.10 shows the fractured surface of a film cast from latex PS/PBA (80/20), prepared by the shot-growth process. There is a contrast between the PS core particles and the PBA coats, the PBA coats appearing to be bound to the PS cores. Figure 5.11 shows a fractured surface of a film cast from latex PS/PBA (80/20) prepared by the seeded-growth process. This micrograph appears to show separation of the PBA coats from the underlying seed latex particles.

Fig. 5.10 Scanning electron micrograph of fractured surface of film cast from PS/PBA (80/20) core-shell latex prepared by the shot-growth method; magnification X 5,000; particle size - 69nm

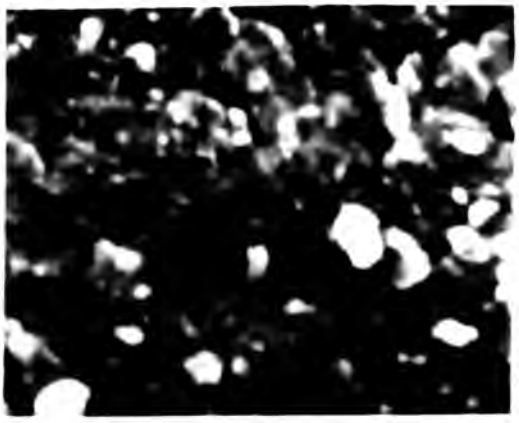


Fig. 5.11 Scanning electron micrograph of fractured surface of film cast from PS/PBA (80/20) core-shell latex prepared by the seeded-growth method; magnification X 5,000; particle size - 78nm

5.8.2 Behaviour of copolymers of styrene and butylacrylate having different copolymer composition and particle morphologies in films from NR latex

The results of this investigation are summarised in Table 5.5 and the various plots shown in Figures 5.12, 5.13 and 5.14. It is evident that overcoating PS particles with PBA appears not to enhance their abilities to reinforce post-vulcanised NR latex films. Various reasons might be suggested for this observation. It seems unlikely that the PBA coats are so weakly bonded to the surface of the PS core particles that they separate from the cores when a high stress is applied. The fact that PBA is not very miscible with NR is a more probable reason.

The method of preparing the copolymer latices appears not to have any significant effect upon the abilities of these copolymer particles to reinforce NR latex films. However, it can be seen from the various plots that the strength properties of the film vulcanisates depend upon the PS/PBA ratio, decreasing with increasing amount of PBA in the copolymers. The tearing of the films was knotty, but the degree of knottiness (as assessed by visual observation) decreased with increasing PBA content in the copolymer particles. From these results, it appears that the PBA is acting as a "plasticiser" in the copolymer particles regardless of the particle morphologies, whether random or core-shell.

One thing that has been clearly demonstrated by this investigation of the behaviour of PS/PBA copolymer particles in the rubber matrix is that the anomalous viscosity changes which are observed when PS and NR latices are blended can be modified by overcoating the PS particles with PBA (see Section 5.14).

Table 5.5 Mechanical properties of NR film vulcanisates containing 10 pphr of S/BA copolymer particles prepared in various ways

Filler	Particle size nm	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}	Nature of tear
None	-	28.7	833	1.34	106	19.5	N
PS	68	30.5	715	2.91	162	15.5	K
PS/PBA (90/10)							
CON	74	31.2	725	2.92	130	17.8	K
SE	75	32.3	737	2.78	138	16.8	K
SH	73	32.6	754	2.84	141	17.4	K
INV	89	28.4	703	2.77	141	17.1	K
PS/PBA (80/20)							
CON	73	30.6	752	2.40	125	16.6	K
SE	78	29.9	728	2.43	146	16.8	K
SH	69	30.6	771	2.51	143	17.6	K
PS/PBA (70/30)							
CON	74	28.8	752	2.47	116	16.5	N
SE	81	28.7	748	2.41	133	17.1	K
SH	72	29.7	764	2.30	130	17.4	K
INV	91	30.0	745	2.47	143	17.5	K
PS/PBA (60/40)							
CON	77	27.4	773	2.19	112	16.6	N
SE	85	27.8	773	2.04	119	17.4	N
SH	70	27.6	778	2.15	119	15.7	N
PS/PBA (50/50)							
CON	74	27.4	782	2.11	111	16.7	N
SE	91	26.9	778	1.86	120	16.8	N
SH	78	26.6	793	2.00	124	16.2	N
INV	93	29.3	778	1.99	133	16.8	K
PBA	76	24.9	787	1.66	108	15.9	N

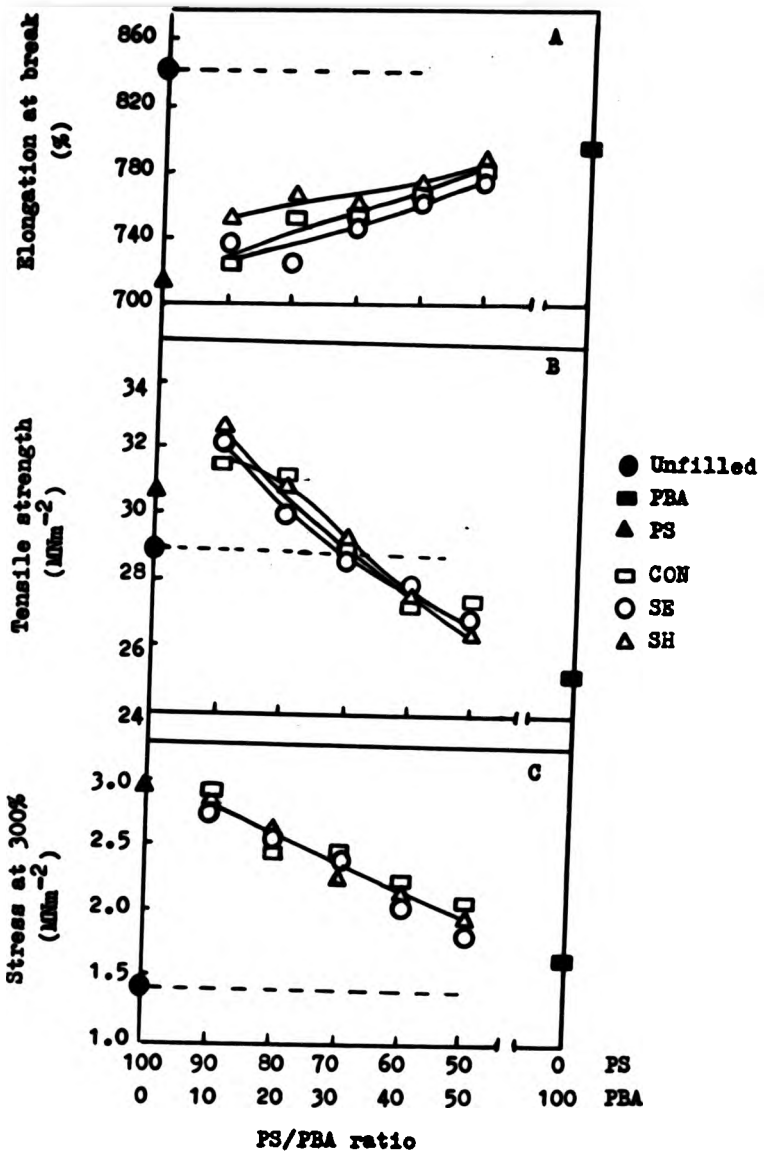


Fig. 5.12 Illustrating mechanical properties of NR film vulcanisates containing styrene/butylacrylate copolymer particles prepared in various ways. Filler loading: 10 pphr. Particle sizes: as given in Table 5.5

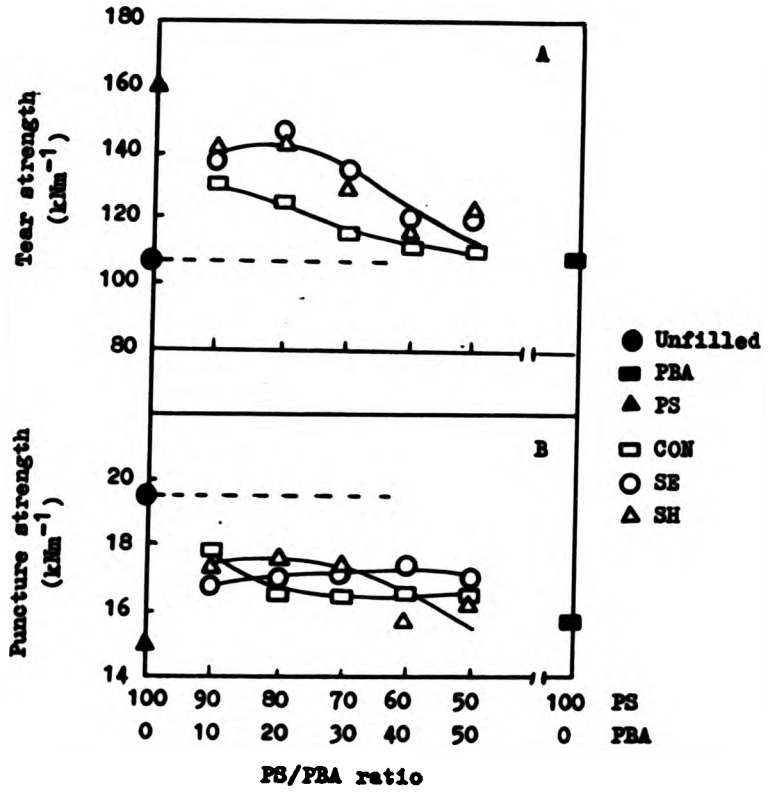


Fig. 5.13 Illustrating mechanical properties of NR film vulcanisates containing styrene/butylacrylate copolymer particles prepared in various ways. Filler loading: 10 pphr. Particle sizes: as given in Table 5.5

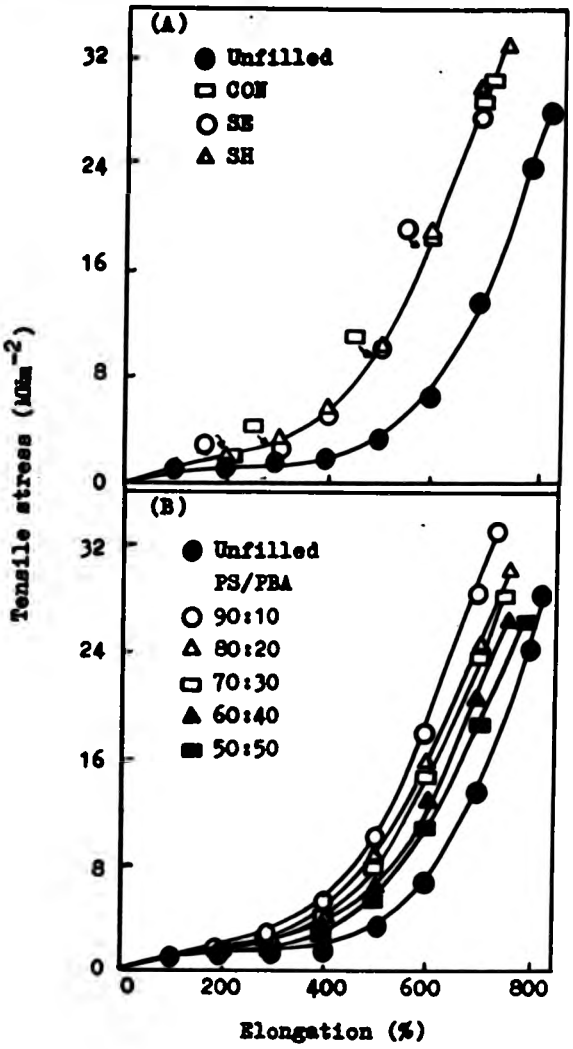


Fig. 5.14 Tensile stress-strain curves for NR film vulcanisates containing (A) styrene/butylacrylate (90/10) copolymer particles prepared in various ways (B) polystyrene/polybutylacrylate (90/10) core-shell particles prepared by the seeded-growth method. Filler loading: 10 pphr. Particle sizes: as given in Table 5.5

5.9 Effect of attempting to promote physical interaction between surface of polymeric filler particles and rubber matrix

The effect of varying the alkyl chain length, and hence tendency to mix with rubber, of the alkyl acrylate/methacrylate comonomer was investigated. The use of VeoVa 10 was also investigated. The effect of using a "linking" monomer, such as allylmethacrylate, to bond the shell to the core covalently in the case of core-shell copolymer particles was also investigated. The results obtained with the various copolymers and core-shell particles are presented and discussed below.

The shot-growth method was used to prepare PS latex particles overcoated with PDA, with PDMA, with POMA and with PVV10. The characteristics of these core-shell polymer particles were similar to those of PS/PBA core-shell latices prepared by shot-growth method.

The mechanical properties of films derived from the blends of NR latex and these filler latices are given in Table 5.6 and Figures 5.15 and 5.16. Unlike particles overcoated with PBA, these particles reinforced the films, particularly the tear strength. The variation of the mechanical properties with copolymer compositions is similar to that of PS/PBA core-shell polymer particles. However, unlike PS/PBA core-shell particles, the PS particles overcoated with the polymers of long-chain acrylates gave higher values of tear strength and tensile strength at relatively lower tensile stress at 300% extension. Since the core-shell polymer particles were prepared in the same way (i.e., by the shot-growth method), the enhancement of tear strength and tensile strength manifested by these overcoated particles can be ascribed to good mixing interaction between the polymer of the long-chain acrylate coat and the rubber matrix in which the core-shell particles were embedded.

It can be seen from Table 5.6 and Figure 5.16A that maximum tear strength values were attainable when PS (80-

Table 5.6 Mechanical properties of NR film vulcanisates containing 10 pphr PS particles overcoated with various polymers

Filler	Particle size nm	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}
None	-	28.7	833	1.34	106	19.5
PS	68	30.5	715	2.91	162	15.5
PS/PDA						
95: 5	72	31.1	715	2.56	163	16.3
90:10	75	33.3	750	2.20	173	17.4
80:20	74	29.0	701	2.24	176	16.3
70:30	76	29.1	689	2.10	164	16.9
50:50	80	25.4	728	1.88	120	16.6
PS/POMA						
95: 5	71	33.6	701	2.72	168	14.6
90:10	74	30.8	722	2.27	169	16.2
80:20	75	29.5	720	2.20	156	16.6
70:30	77	27.7	712	2.12	150	16.8
PS/PDMA						
95: 5	73	30.1	701	2.50	160	15.6
90/10	75	32.3	725	2.35	163	15.8
80:20	75	28.0	730	2.15	170	14.7
70:30	76	27.7	748	2.00	172	14.7
PS/PVV10						
95: 5	70	34.2	731	2.92	191	14.2
90:10	72	33.2	730	2.77	191	14.0
80:20	75	34.8	733	2.56	175	14.4
70:30	74	35.0	770	2.29	172	15.3
50:50	78	32.0	803	1.92	165	16.4

Nature of tearing: all the filled films showed knotty tearing

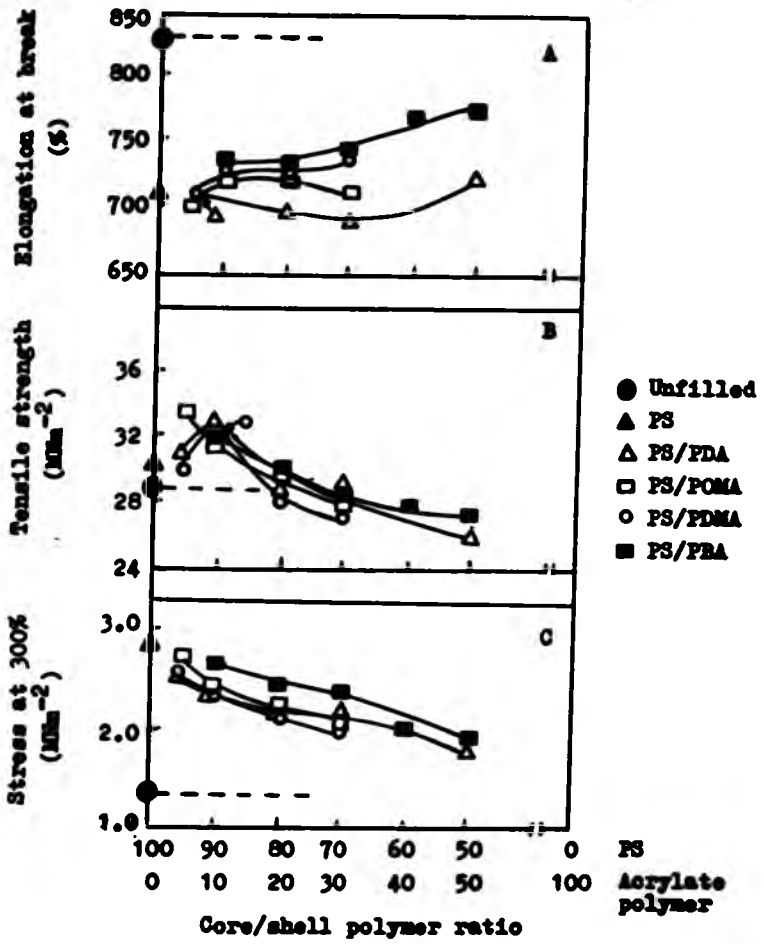


Fig. 5.15 Illustrating mechanical properties of NR film vulcanisates containing PS particles overcoated with a range of acrylate polymers prepared by the shot-growth method. Filler loading: 10 pphr. Particle sizes: PS/PBA core-shell - as given in Table 5.5; others - as given in Table 5.6

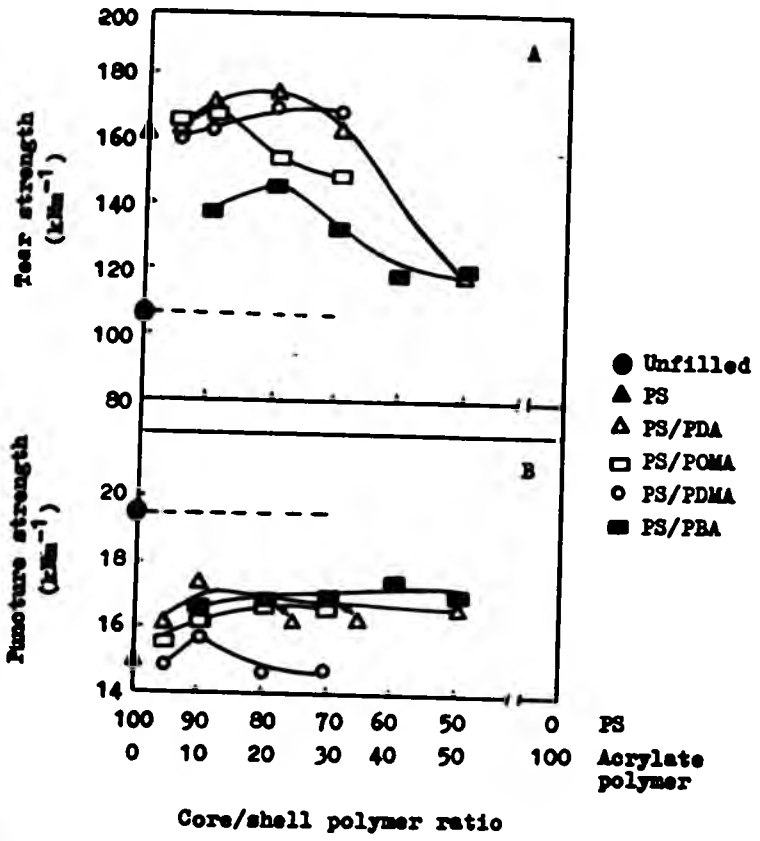


Fig. 5.16 Illustrating mechanical properties of NR film vulcanisates containing PS particles overcoated with a range of acrylate polymers prepared by the shot-growth method. Filler loading: 10 pphr. Particle sizes: PS/PBA core-shell - as given in Table 5.5; others - as given in Table 5.6

Table 5.7 Effect of loading of PS particles overcoated with various polymers upon mechanical properties of NR film vulcanisates

Filler	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}	Nature of tear
None	28.7	833	1.34	106	19.5	N
PS						
10 pphr	30.5	715	2.91	162	15.0	K
20 pphr	26.9	618	3.70	167	12.9	K
30 pphr	26.2	600	4.38	156	12.0	K
PS/PBA (80/20)						
10 pphr	29.9	728	2.43	146	16.8	K
20 pphr	25.7	626	3.45	156	12.2	K
30 pphr	24.2	615	4.20	140	10.7	K
PS/PDA (90/10)						
10 pphr	33.3	750	2.20	173	17.4	K
20 pphr	29.6	720	3.07	175	15.0	K
30 pphr	28.0	707	3.61	167	11.8	K
PS/PCMA (90/10)						
10 pphr	30.8	722	2.27	169	16.2	K
20 pphr	28.3	734	2.54	174	15.2	K
30 pphr	27.6	719	3.05	166	14.9	K
PS/PVV10 (90/10)						
10 pphr	33.2	730	2.77	191	14.0	K
20 pphr	31.0	708	3.39	180	13.7	K
30 pphr	28.8	695	3.63	159	12.9	K

Particle sizes: PS - 68nm, PS/PBA (80/20) - 69nm, PS/PDA (90/10) - 74nm, PS/PCMA (90/10) - 74nm, PS/PVV10 (90/10) - 72nm

K - knotty, N - not knotty

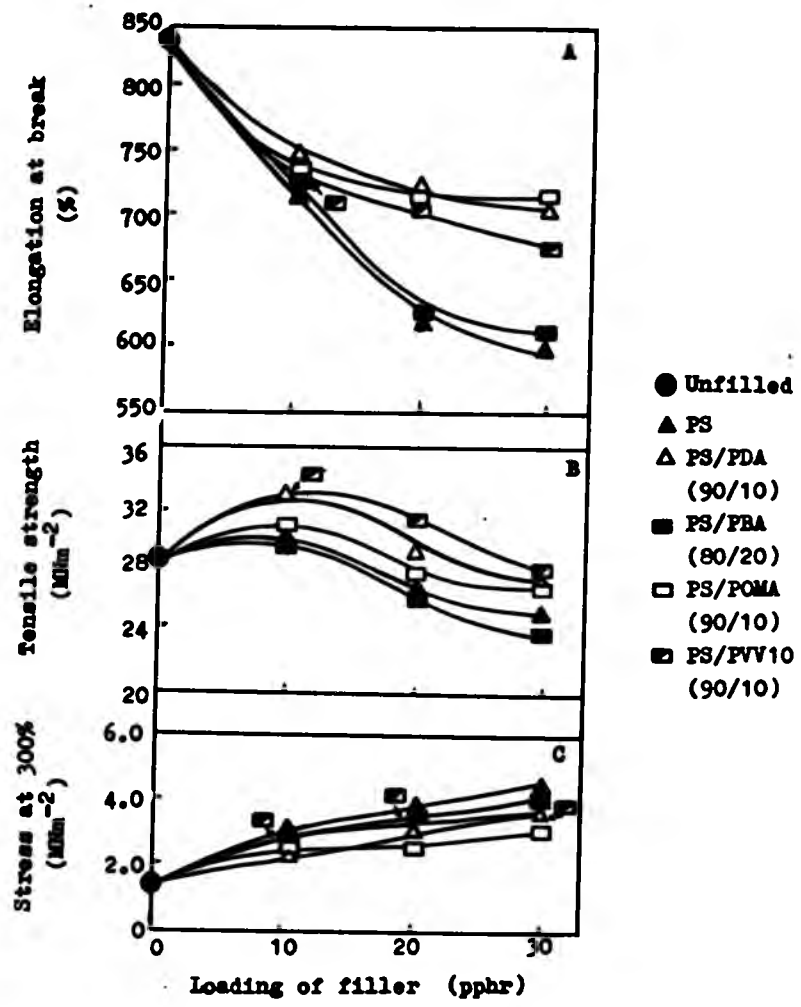


Fig. 5.17 Effect of loading of PS particles overcoated with various polymers upon mechanical properties of NR film vulcanisates. Particle sizes: as given in Table 5.7

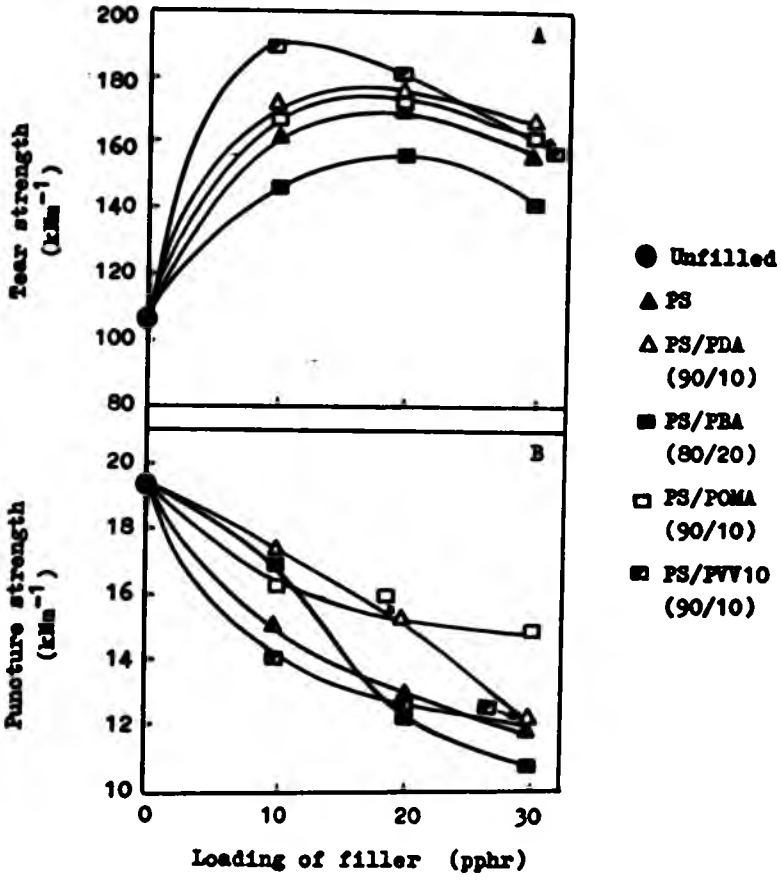


Fig. 5.18 Effect of loading of PS particles overcoated with various polymers upon mechanical properties of NR film vulcanisates. Particle sizes: as given in Table 5.7

90)/acrylate polymer (20-10) core-shell particles were used in most cases. When PVV10 was used as the coating polymer, the tear strengths were considerably higher than when the long-chain acrylate polymers were used as the coating polymer (Table 5.6). However, the values of stress at 300% extension were higher as well. Particles overcoated with PVV10 gave higher tensile strengths, whereas the particles overcoated with polymers of long-chain acrylates gave better puncture strength, particularly when PS/PDA (90/10) core-shell particles were used.

The effects of the loading of the various core-shell polymer particles upon the mechanical properties of NR film vulcanisates are given in Table 5.7 and shown in Figures 5.17 and 5.18. The tear strength and tensile strength pass through a maximum and then decrease. The stress at 300% extension increases steadily with increasing filler loading, whilst elongation at break decreases. The effect of filler loading is discussed in detail in Section 5.13.

The possibility of enhancing the level of reinforcement by the core-shell particles by chemically bonding the coating polymer to the surface of the PS core particles using allylmethacrylate was investigated. The mechanical properties of the films obtained from NR latex containing core-shell particles of this type are given in Table 5.8. Figures 5.19 and 5.20 show the effects of various loadings of PS/PAMA/PDA (85/5/10) core-shell particles upon the mechanical properties of the film vulcanisates. Although these core-shell particles appear to give consistently higher tear strength and puncture strength values without an appreciable increase in the other strength properties, the differences are not sufficiently significant to justify the trouble of bonding the PDA coat on to the surface of the PS core particles. Similarly, bonding the PVV10 coat on to the surface of PS particles did not enhance the level of reinforcement above that conferred by core-shell particles whose coats are not

Table 5.8 Effect of chemically bonding PDA and PVV10 shells to PS core particles upon the mechanical properties of NR film vulcanisates (filler loading: 10 pphr)

Filler	Particle size nm	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}
None	-	28.7	833	1.34	106	19.5
PS	68	30.5	715	2.91	162	15.0
PS/PDA (90/10)	75	33.3	750	2.20	173	17.4
PS/PVV10 (90/10)	72	33.2	730	2.77	191	14.0
PS/PAMA/PDA						
88: 2: 10	72	30.0	723	2.35	168	16.6
85: 5: 10	76	29.3	701	2.23	179	18.1
80: 10: 10	75	30.2	707	2.14	180	17.9
70: 20: 10	76	30.3	708	2.03	170	18.1
60: 30: 10	78	28.3	722	1.92	156	18.5
PS/PAMA/PVV10						
85: 5: 10	74	30.6	710	2.82	175	15.4
80: 10: 10	75	33.7	776	2.36	191	14.9
PS/PAMA/PDA (85/5/10)	76					
20 pphr	-	30.1	660	3.36	183	14.3
30 pphr	-	26.1	626	3.70	169	13.2

Nature of tearing: all the filled films showed knotty tearing

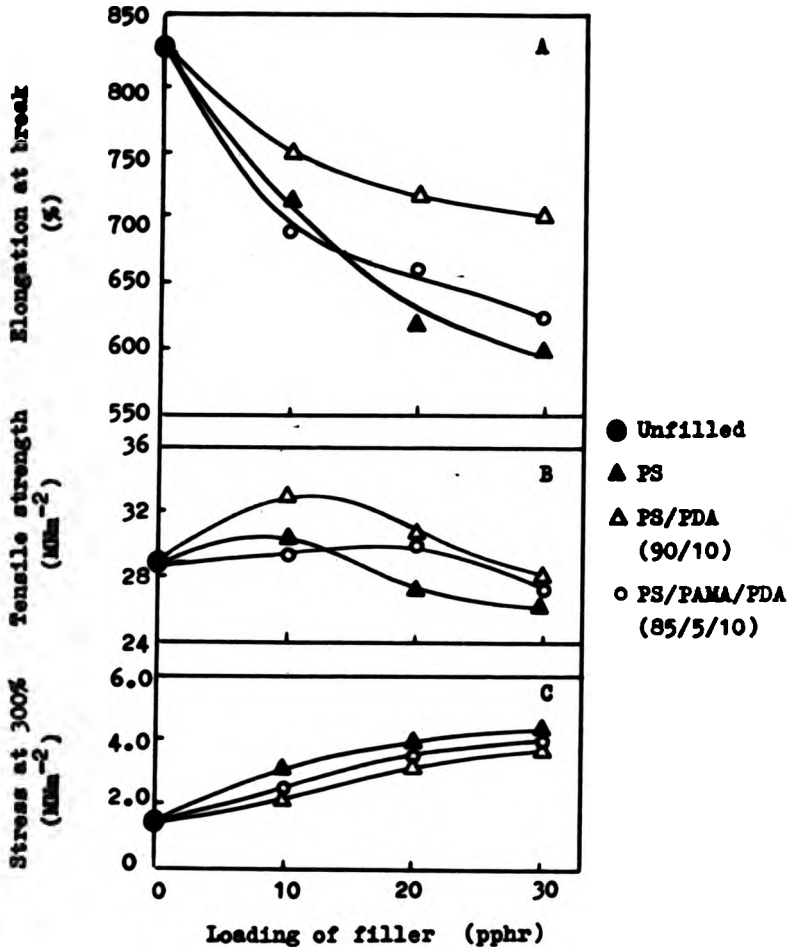


Fig. 5.19 Illustrating effect of linking PDA shell to the surface of PS core particles using allylmethacrylate upon ability of PS/PDA core-shell particles to reinforce NR film vulcanisates. Particle sizes: PS - 68nm, PS/PDA (90/10) - 75nm, PS/PAMA/PDA (85/5/10) - 76nm

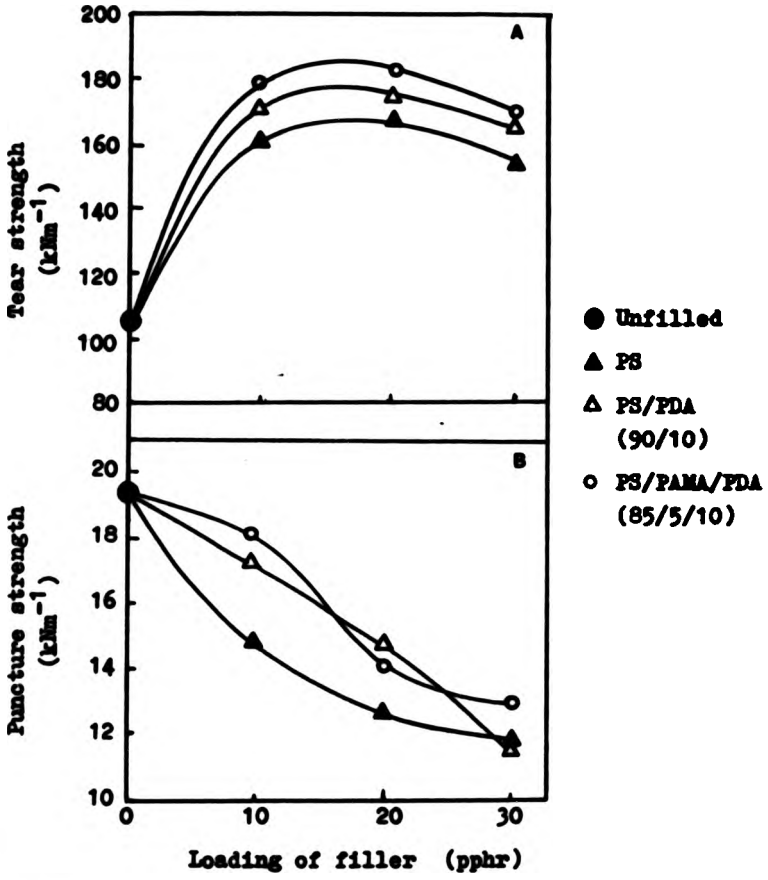


Fig. 5.20 Illustrating effect of linking PDA shell to the surface of PS core particles using allylmethacrylate upon ability of PS/PDA core-shell particles to reinforce NR film vulcanisates. Particle sizes: PS - 68nm, PS/PDA (90/10) - 75nm, PS/PAMA/PDA (85/5/10) - 76nm

bonded. This is perhaps not surprising, as the core-shell particles whose shells were not bonded to the cores were prepared by the shot-growth method, and as such, would be expected to be strongly bonded to the surface of the core-particle as remarked before. However, if the tear strength values are compared with the value obtained for uncoated PS particles, the core-shell particles appear to give better enhancement of tear strength. For instance, tear strength values of 162, 173 and 180 kNm^{-1} were obtained for PS, PS/PDA (90/10) and PS/PAMA/PDA (80/10/10) core-shell particles respectively, and tear strength values of 191 and 191 kNm^{-1} were obtained for PS/PVV10 (90/10) and PS/PAMA/PVV10 (80/10/10) core-shell particles respectively. To obtain a proper indication of the significances of these results, statistical paired comparison tests were employed using the t-test and the Wilcoxon test. At the 5% level of significance (i.e., there are about 5 chances in 100 that the wrong decision has been made, i.e., 95% confidence that the correct decision has been made), it was found that there was no significant difference between the enhancement of tear strength by coated PS particles prepared with and without a chemical bonding agent. However, there was a significant difference between the enhancement of tear strength by the overcoated particles and the uncoated PS particles.

Figures 5.21 and 5.22 demonstrate the effect of increasing the level of the bonding monomer upon the level of reinforcement conferred by these core-shell particles. It can be seen that the level of bonding monomer has little effect upon reinforcement.

It is evident from the results obtained using PS particles overcoated with polymers of long-chain acrylates and with PVV10 bonded to the surface of filler particles that the overcoating plays a very important role in enhancing reinforcement. The observed increase in the level of enhancement of the tear strength and tensile strength is believed to be mainly due to improved adhesion between the filler and the rubber matrix in which

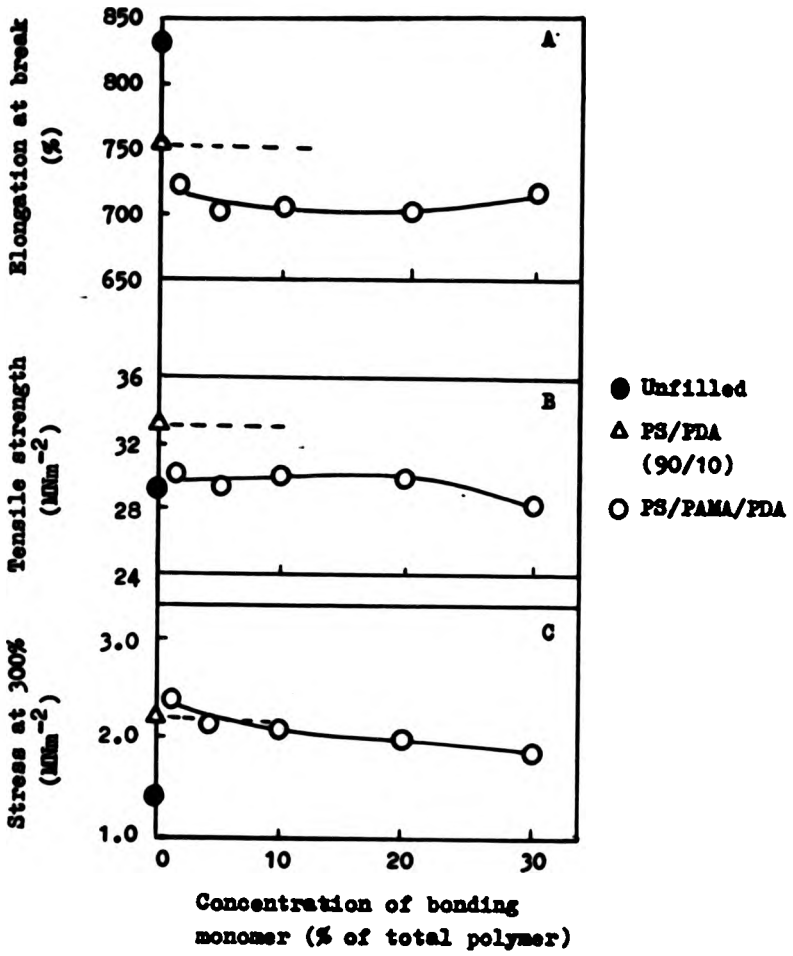


Fig. 5.21 Illustrating effect of concentration of allylmethacrylate used to bond PDA shell on to the surface of PS core particles upon ability of PS/PDA core-shell particles to reinforce NR film vulcanisates. Filler loading: 10 pphr. Particle sizes: as given in Table 5.8

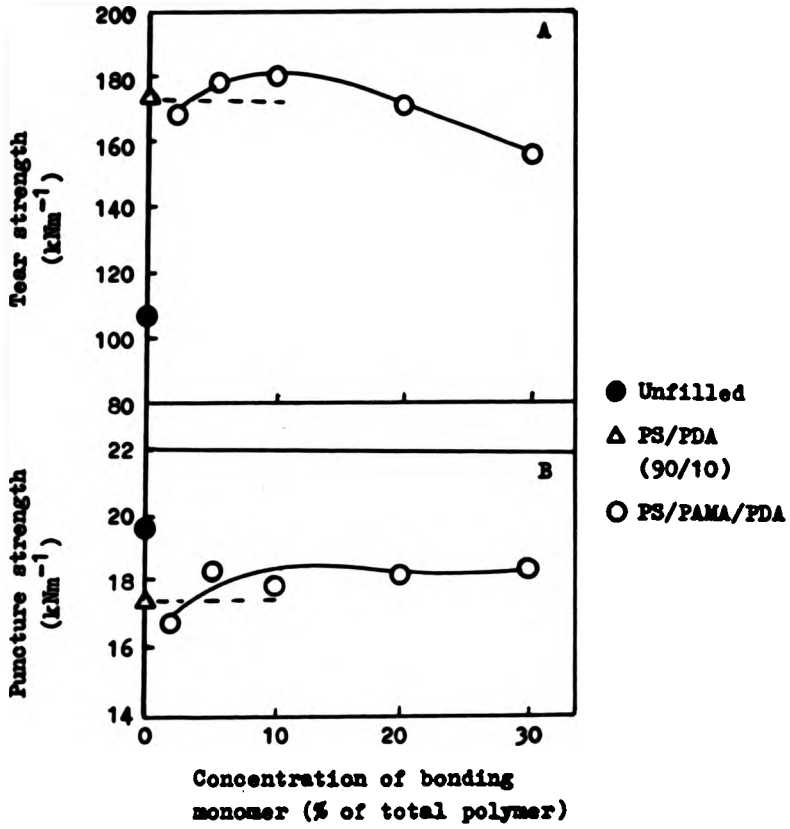


Fig. 5.22 Illustrating effect of concentration of allylmethacrylate used to bond PDA shell on to the surface of PS core particles upon ability of PS/PDA core-shell particles to reinforce NR film vulcanisates. Filler loading: 10 pphr. Particle sizes: as given in Table 5.8

they were embedded. These strength values may be further enhanced because of the ability of these core-shell particles to yield and absorb energy, thus delaying the onset of crack propagation. Energy dissipation is assisted by the efficient transmission of the applied stress through the elastic polymer coats which are bonded to the rigid core-particles, as well as by the presence of phase mixing at the interface between core-shell particles and the rubber phase.

Of particular interest is the nature of the tear propagation of the films containing these overcoated particles. In all cases, the tear proceeded in a stick-slip or knotty manner to leave rough irregular torn surfaces. The effect was particularly pronounced when 10-20 pphr of PS/PAMA/PDA (85/5/10) and PS/PVV10 (90/10) particles were used. This explains why high tear strength values were attainable with these particles. The enhancement of tear strength associated with stick-slip or knotty tearing stems from the increase in the effective diameter at the tip of the tear. This effective diameter, d, is defined by equation 5.1

$$T = ed \qquad 5.1$$

where T is the tearing energy and e is the strain energy per unit volume required to break the rubber in simple extension (9). The dissipation of energy resulting from multiple internal failures at the filler-rubber interfaces, and the greater distance travelled by the rupture path can both contribute to an increase in tearing energy produced by reinforcing fillers. However, for this increase in tearing energy to result, it is necessary that failures at the filler-rubber interface should not occur until high stresses are reached. If the failure takes place at low stresses, the rubber ruptures from the resultant flaws. Thus, in order to confer effective reinforcement, the filler particles must have good adhesion to the rubber matrix in which they are embedded.

5.10 Effect of polystyrene particles whose surfaces had been functionalised to make them co-vulcanisable with the rubber matrix

The possibility of enhancing the level of reinforcement conferred by PS particles by promoting chemical interaction between the surface of the filler particles and the rubber matrix was investigated. This aspect of the investigation was carried out by functionalising the surface of the PS particles with allylmethacrylate and with isoprene units as outlined in the experimental section. As previously stated in Chapter Four (Section 4.2.6), it was expected that the resulting copolymers would contain unreacted carbon-carbon double bonds and α-methylene hydrogen atoms, which would permit the molecules at the exterior of the filler particle subsequently to co-vulcanise with the NR matrix during the sulphur vulcanisation reaction.

5.10.1 Results for determination of residual unsaturation in latices containing particles whose surfaces had been functionalised

The number of unreacted double bonds on the surface of the functionalised particles was determined using Wijs' method as described in the experimental section (4.3.1.7). The results obtained for the concentrations of the unreacted double bonds together with the "expected values" are given in Table 5.9. The "expected values" are the values assuming one double bond per residual functionalising molecule. As stated before, Wijs' method uses iodine monochloride, and is the most common method used for the determination of unsaturation in polymers. In Table 5.9, the unsaturation is expressed in terms of the so called "iodine value", which is defined as the number of grams of iodine which has combined with 100 grams of sample. Within the limits of experimental error, the observed iodine value for the various particles agreed

Table 5.9 Results for determination of residual unsaturation in PS particles whose surfaces had been functionalised

Polymer	Iodine value (g I_2/100g sample)		*Degree of unsaturation (%)
	Observed	Expected	
PS	0.26	0	-
PI	359	372	96.5
PAMA	195	198	98.5
PS/PI			
98: 2	7.30	7.45	98.1
95: 5	18.2	18.6	98.0
90:10	36.5	37.2	98.0
80:20	72.0	74.5	96.6
70:30	108	111	97.0
60:40	141	149	94.6
50:50	177	186	95.1
PS/PAMA			
98: 2	3.91	3.96	98.7
95: 5	9.81	9.90	99.0
90:10	19.3	19.8	97.6
80:20	39.2	39.6	98.9
70:30	58.9	59.4	99.3
60:40	78.5	79.2	97.1
50:50	98.1	99.0	99.1

$$\text{*Degree of unsaturation} = \frac{\text{observed iodine value}}{\text{expected iodine value}} \times 100$$

with the expected values, indicating that there was little loss in the functional monomers beyond the one double bond per molecule which would result from linear chain polymerisation. However, it was found, as given in Table 5.9, that the unsaturation in the PS/PAMA copolymers were closer to the expected value than were those for the PS/PI copolymers, suggesting some type of interlinkage between the polyisoprene chains may have occurred. The resulting copolymers were also dissolved in toluene to see if any crosslinking by the functional monomers had taken place during the copolymerisation. The PS/PAMA core-shell particles dissolved completely in toluene, whereas the PS/PI core-shell particles did not dissolve completely, suggesting once again that some type of interlinkage between the polyisoprene chains had occured.

5.10.2 Mechanical properties of films from NR latex containing particles whose surfaces had been functionalised

The effects of the PS particles whose surfaces had been functionalised upon the mechanical properties of films from NR latex are given in Table 5.10 and Figures 5.23 and 5.24. It can be seen from Table 5.10 and Figure 5.24A that the tear strength of the films containing PS/PAMA particles was enhanced, particularly at high concentration of double bonds (i.e., high contents of PAMA in the copolymers) on the particle surface, although the stress at 300% extension was relatively low. The highest tear strength (183 ± 12 kNm^{-1}), when PS/PAMA (70/30) filler was used) obtained with these particles was higher than that obtained with the unmodified PS particles (162 ± 12 kNm^{-1}, stress at 300% extension being lower. (2.31 ± 0.08 and 2.91 ± 0.15 MNm^{-2} respectively). These particles also imparted better puncture strength. There was no significant difference in the elongation at break and tensile strengths. In the case of the PS/PI core-shell particles, there was no significant difference between the

Table 5.10 Mechanical properties of NR film vulcanisates containing 10 pphr PS particles whose surfaces had been functionalised with allylmethacrylate and isoprene units

Filler	Particle size nm	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}
None	-	28.7	833	1.34	106	19.5
PS	68	30.5	715	2.91	162	15.5
PS/PAMA						
98: 2	70	28.9	690	2.56	160	15.0
95: 5	71	30.1	701	2.50	164	14.7
90:10	74	34.0	723	2.45	171	16.9
80:20	75	31.8	698	2.44	176	18.5
70:30	76	30.8	692	2.31	183	18.0
60:40	75	31.0	740	2.19	174	19.0
50:50	77	30.8	740	2.22	180	19.6
PS/PI						
98: 2	72	30.0	692	2.51	159	16.0
95: 5	72	31.6	700	2.50	169	15.6
90:10	75	31.7	708	2.41	167	16.3
80:20	74	35.2	731	2.32	168	16.1
70:30	77	32.2	732	2.05	158	15.8
60:40	76	28.1	755	1.87	145	16.9
50:50	78	26.7	761	1.80	139	17.2
PS/PI (80/20)	75					
20 pphr	-	28.8	700	2.72	173	15.0
30 pphr	-	26.0	634	3.52	166	12.2

Nature of tearing: all the filled films showed knotty tearing with the exception of films containing PS/PI (50/50) particles

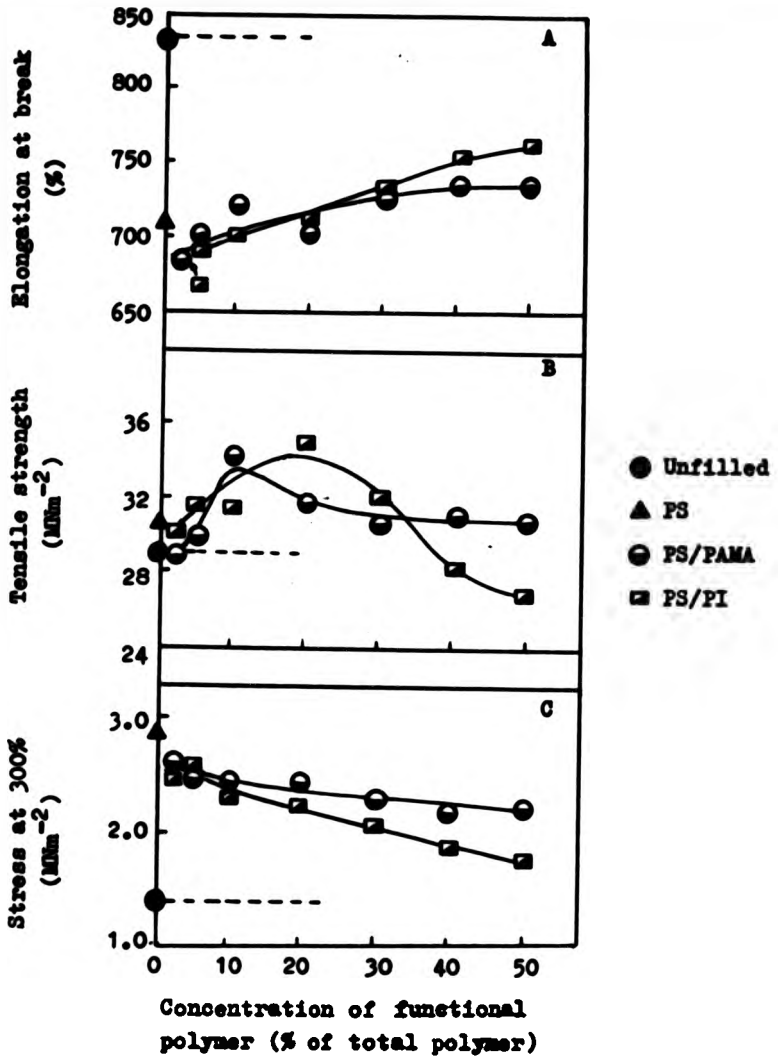


Fig. 5.23 Illustrating mechanical properties of NR film vulcanisates containing PS particles whose surfaces had been functionalised with allylmethacrylate and isoprene units. Filler loading: 10 pphr. Particle sizes: as given in Table 5.9

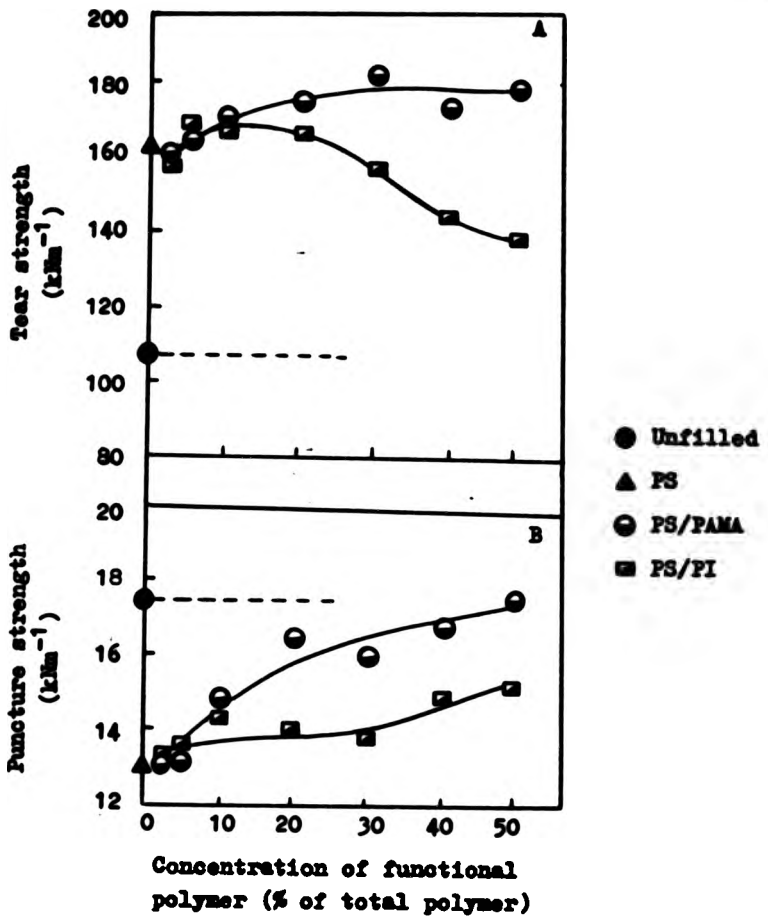


Fig. 5.24 Illustrating mechanical properties of NR film vulcanisates containing PS particles whose surfaces had been functionalised with allylmethacrylate and isoprene units. Filler loading: 10 pphr. Particle sizes: as given in Table 5.9

tear strengths of films containing these particles and of films containing the unmodified PS particles.

These results show that PS/PAMA core-shell particles appear to give better enhancement of tear strength and puncture strength than do PS/PI core-shell particles (Figure 5.24B). However, when a paired comparison test (using t-test at significant level of 5%) was carried out on the highest tear strength and the corresponding puncture strength values obtained with these particles (i.e., PS/PAMA (70/30) and PS/PI (80/20)), significant difference was found in the puncture strength but not in the tear strength. On the other hand, when the same statistical test was carried out on the value of tear strength and puncture strength obtained with these particles and with the uncoated PS particles, the difference between the PS/PAMA (70/30) core-shell particles and the uncoated PS particles was significant, but the difference between the PS/PI (80/20) core-shell particles and the PS particles was not.

The reason for the slight difference in the behaviour of PS/PAMA and PS/PI core-shell particles in the rubber matrix is not entirely clear. If anything, one would expect PS/PI core-shell particles to confer better enhancement of tear strength. Apart from the presence of carbon-carbon double bonds and α-methylene hydrogen atoms in the shell which are expected subsequently to cause the molecules of the core-shell filler particles to co-vulcanise with NR during sulphur vulcanisation reaction in both cases, one would expect PS/PI core-shell particles to manifest a greater tendency to mix with the rubber matrix because of the similarity in the chemical structure of the synthetic PI and NR. However, the presence of interlinkages between polyisoprene chains (indicated by slightly lower iodine values) would be expected to reduce the mixing tendency and perhaps also the tendency to chemical interaction (i.e., co-vulcanisation) between the surface of the particles and the rubber matrix in which they are embedded. The result of this effect would be a

reduction of the physical and chemical adhesion between the particles and the rubber matrix. The effect of the poorer mixing interaction between the PI shell and the rubber matrix in which the PS/PI core-shell particles were embedded upon mechanical properties of the film vulcanisates is more pronounced when the core-shell particles contained high concentrations (>30% of the total polymer) of the polyisoprene shell. However, the reduction in rigidity of the copolymer particles as the concentration of polyisoprene in the copolymer increased would also be expected to affect adversely the ability of the core-shell particles to reinforce the film vulcanisates.

5.11 Results of examination of fractured tensile test-pieces by scanning electron microscope

Typical scanning electron micrographs of the fractured surfaces of tensile test-pieces are shown in Figure 5.25. Initially the pictures were taken at low magnification (2,000-3,000X) but the filler particles were not clearly visible. The pictures were therefore taken at higher magnification (5,000X) in order that the particles could be seen clearly. The result of this is poor resolution and cloudy pictures. (Pictures taken at higher magnification (6,000-10,000X) were even worse). However, these pictures appear to confirm that the films containing uncoated PS particles show little tendency to bond to the rubber matrix. Cavities from which particles had been pulled out during the tensile test are visible, but a number of particles appear to be torn loose on the broken surface. At the other extreme, PS particles overcoated with polyVeoVa 10 show a tendency to remain bonded to the rubber matrix. The evidence of these micrographs appears to confirm the interpretation which has been made of the mechanical properties, particularly tear strength, of the rubber films containing the filler particles.

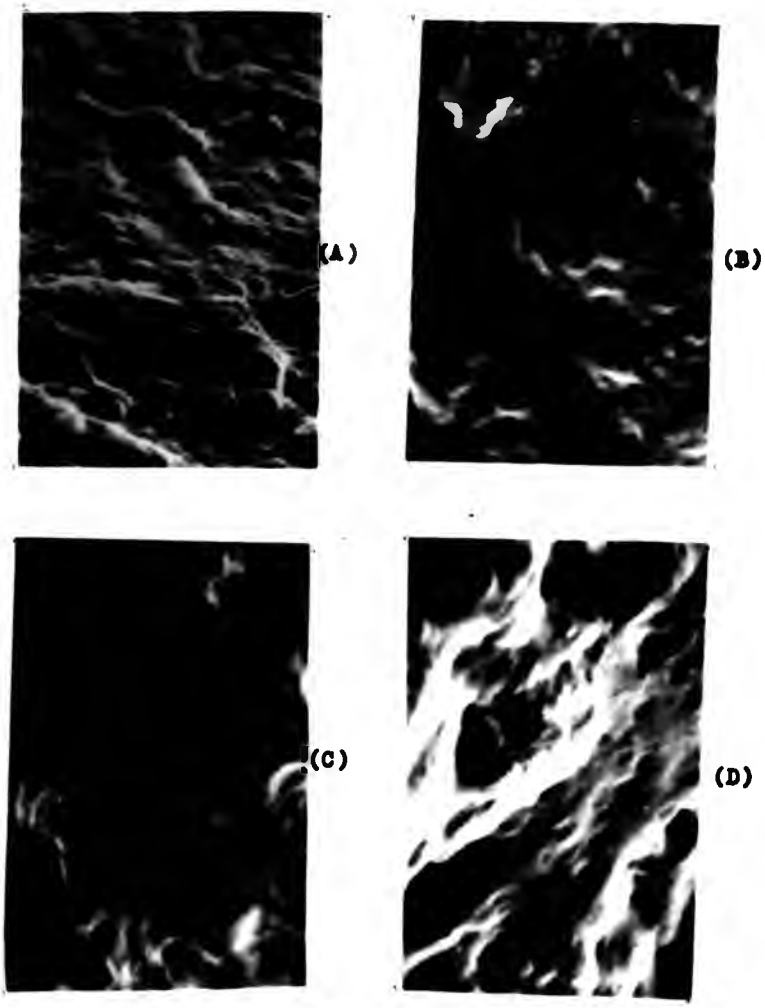


Fig. 5.25 Scanning electron micrographs of ruptured surfaces of tensile test-pieces of NR film vulcanisates containing 10 pphr of various fillers. Fillers: (A) PS particles (68nm); (B) PS/PDA (90/10) core-shell particles (75nm); (C) PS/PAMA (80/20) core-shell particles (75nm); (D) PS/PVP10 (90/10) core-shell particles (72nm). Magnification X 5,000

5.12 Further discussion of effects of physical and chemical interactions between filler and matrix upon mechanical reinforcement of NR film vulcanisates

In order to assess the relative importance of the effects of promoting physical interaction and chemical interaction between the filler particles and rubber matrix in which they were embedded, the mechanical properties of NR film vulcanisates containing 10 pphr of (I) PS/PAMA/PDA and PS/PVV10; and (II) PS/PAMA core-shell polymer particles having different copolymer compostions are compared. The results obtained with PS/PAMA/PDA core-shell particles of this type are presented in order to see the effect of using a bonding monomer to bind the shell to the core covalently in the case of PS/PDA core-shell copolymer particles. It should be recalled here that the copolymer particles of type (I) manifested better reinforcement than all the other PS particles overcoated with various polymers of long-chain acrylates, whilst PS particles functionalised with allylmethacrylate units manifested better reinforcement than PS particles functionalised with isoprene units, with respect to tear strength and puncture strength. It is therefore appropriate to compare the effects of filler particles of type (I) with the effects of filler particles of type (II).

5.12.1 Results of investigation of extractability of filler particles from NR film vulcanisates

In order to gain some indication of the nature of the bonding between the various filler particles and the rubber matrix in which they have been embedded, the filled vulcanisates were extracted with toluene as described in Section 4.3.1.7. The filler particles themselves were completely soluble in toluene under the conditions used.

The results of the solvent extraction experiments are given in Table 5.11. The total extract represents the

TABLE 5.11 Results of investigation of extractabilty of polymeric filler particles from NR film vulcanisates

Filler	Total extract % by wt.	Filler extracted % by wt.
None	3.35	-
PS	11.80	98.9
PS/PBA (80/20)	11.68	97.5
PS/PAMA/PDA(85/5/10)	11.70	97.8
PS/PVV10 (90/10)	7.62	48.2
PS/PAMA	5.24	21.7

filler loading : 8.54% by weight (ca. 10 pphr)

amount of filler and curatives extractable. The amount of filler extracted was determined by subtracting the amount of curatives extractable from the total extractable mate-

rial. The amount of filler extracted was then expressed as a percentage of the filler loading in the sample. The solvent extraction results for the films which contained PS, PS/PBA (80/20) and PS/PAMA/PDA (85/5/10) particles indicate that, within the limits of experimental error, virtually all the filler is solvent-extractable after vulcanisation. The result for the film containing PS/PVV10 (90/10) particles shows that 50% of the weight of the filler particles was chemically bonded to the rubber. The result for the film containing PS/PAMA (80/20) particles shows that almost all the filler was chemically bonded to the rubber. It is not clear at present whether the amount of unextractable PS/PVV10 (90/10) filler is actually chemically bonded to the rubber or is merely difficult to extract completely. However, it is at least the case that the two sets of core-shell filler particles under consideration (i.e., (I) PS/PVV10 (90/10) and PS/PAMA/PDA (85/5/10); (II) PS/PAMA (80/20)) show marked variation in the extent of bonding between the filler and rubber matrix in which they were embedded.

5.12.2 Discussion of results for mechanical properties

Figures 5.26 and 5.27 demonstrate the effects of increasing the proportion of coating polymer in PS/PAMA/PDA, PS/PVV10 and PS/PAMA core-shell particles upon the mechanical properties of NR film vulcanisates containing these particles. In the case of the PS/PAMA/PDA core-shell filler particles the concentration of coating polymer is taken as the total amount of PAMA and PDA in the terpolymers, the concentration of the latter being kept constant at 10% (of total polymer).

From the various plots, it can be seen that the tear strength of the film vulcanisates containing PS/PAMA core-shell particles increased steadily as the amount of PAMA in the copolymers increased. The film vulcanisates containing

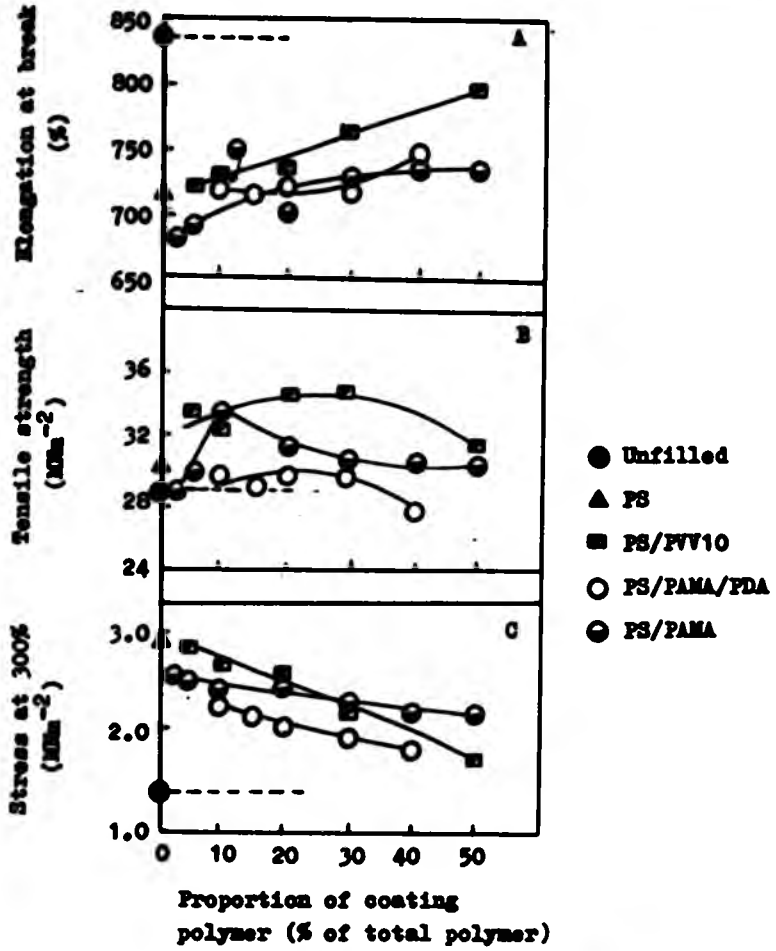


Fig. 5.26 Comparison of effect of promoting mixing interaction and chemical interaction between surface of PS particles and NR matrix. Filler loading: 10 pphr; PVV10 and PAMA are referred to as coating polymers. Particle sizes: PS - 68nm; PS/PVV10, PS/PAMA/PDA and PS/PAMA - as given in Tables 5.6, 5.8 and 5.10 respectively

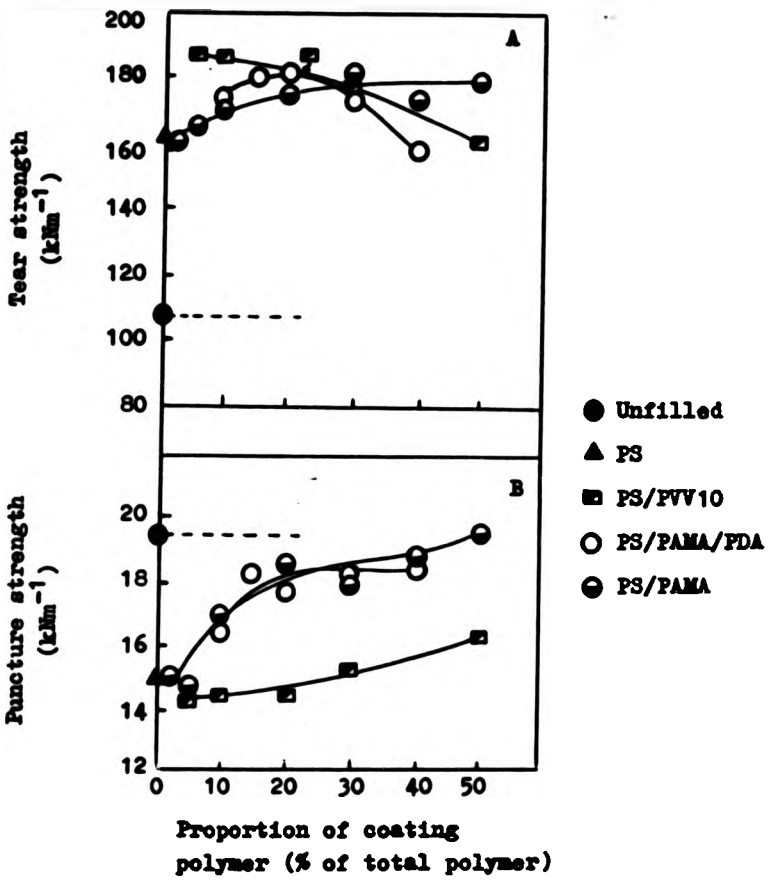


Fig. 5.27 Comparison of effect of promoting mixing interaction and chemical interaction between surface of PS particles and NR matrix. Filler loading: 10 pphr; PVV10 and PAMA are referred to as coating polymers. Particle sizes: PS - 68nm; PS/PVV10, PS/PAMA/PDA and PS/PAMA - as given in Tables 5.6, 5.8 and 5.10 respectively

PS/PVV10 core-shell particles show maximum tear strength value when the core-shell particles contained 5-10% of PVV10 coat, and then decreased. In the case of the PS/PAMA/PDA core-shell particles, maximum tear strength value was attained when PS/PAMA/PDA (80/10/10) core-shell particles were used. The various filled vulcanisates showed steady increases in puncture strength as the amount of the coating polymer in the core-shell particles embedded in the films increased, but PS/PAMA core-shell particles appear to give consistently higher values, whilst PS/PVV10 core-shell particles give consistently lower values. The maximum tensile strength obtained with the various core-shell particles was highest for films which contained the PS/PVV10 core-shell particles.

Attempts were made to compare the effects of the loading of these filler particles upon their abilities to reinforce films from NR latex, using core-shell particles which gave optimum tear strength from each group. Unfortunately, it was not possible to obtain homogeneous films from NR latex containing PS/PAMA core-shell particles at loadings above 10 pphr, because the films cracked on drying.

From the results obtained for the various filled vulcanisates, it is clear that the level of reinforcement imparted by PS particles in NR latex film vulcanisates can be enhanced by promoting physical and chemical interaction between the PS particles and the rubber matrix either by providing the particles with a surface (PVV10 or PDA coat) which tends to mix well with the rubber matrix or by providing the particles with a surface (PAMA coat) which reacts chemically with the rubber matrix. However, from these results, it is not entirely clear what advantage the one procedure may have over the other as far as effects upon the ability of the modified particles to reinforce post-vulcanised NR latex films are concerned.

In order to ascertain the combined effect of physical and chemical interactions, the behaviour of PS particles overcoated with copolymers of dodecylacrylate and

allylmethacrylate was also investigated. The mechanical properties of films filled with these particles were similar to those filled with PS/PDA core-shell particles. Thus, it appears that overcoating PS particles in this way confers no advantages over the use of either coating procedure separately.

As has already been noted in Chapter Two (Section 2.1.3.1B), experiments with both polystyrene particles and styrene-butadiene copolymer particles as model fillers in SBR vulcanisates have been carried out by Morton et al. (10). The results have shown that covalent chemical bonding between rubber and filler is not a necessary prerequisite for the manifestation of reinforcement in rubber vulcanisates. In carefully-controlled experiments, they could show that, in the case of the PS particles, no chemical bonds were formed during vulcanisation. As stated previously, this was to be expected, because the PS chain molecule has no olefinic double bonds and hence is not reactive. By copolymerisation with 10% butadiene, chemical unsaturation was introduced into the polymer chain, and particles made from these copolymers show evidence of being chemically bonded to the rubber. The tensile strength results for the various filled vulcanisates led to the conclusion that rubber-filler bonds have no effect upon reinforcement. The tear strengths and puncture strengths of the filled vulcanisates were not determined. However, as has also been stated before (Section 2.1.3.2B), in another paper, Morton et al. (5) reported that better adhesion between rubber and filler leads to higher strength. This is in complete agreement with the findings in the present investigation.

In the case of vulcanisates filled with carbon black, different views have been expressed by various workers concerning the nature of bonding between the filler particles and the rubber matrix, and also upon the relative importance of each type of filled systems. As remarked in Chapter Two of this thesis (Section 2.1.3),

both physical bonding (11-18) e.g., a type of labile adsorption, and chemical bonding (19-38), have been invoked in the literature to explain the phenomenon of 'bound rubber', and each effect is regarded in the literature as being capable of contributing to the reinforcement of rubber vulcanisates by carbon blacks. To the extent that chemical interactions do occur, they may usefully be regarded as contributing to the effectively crosslink density of the elastomer network (10); indeed some at least of the increase in modulus associated with reinforcement in carbon black filled vulcanisates can be attributed to this cause.

5.13 Effect of filler loading

At an early stage of the present work, the effects of loading of PS and PMMA fillers (of particle sizes 68nm and 69nm respectively) upon the mechanical reinforcement of films derived from NR latex were investigated. The effects of the loadings of these filler particles upon the mechanical properties of films obtained from NR latex are shown in Figures 5.28 and 5.29. As expected (see Section 5.16.3), the stress at 300% extension of the vulcanisates increase with increasing filler loading while elongation at break decreased. The tensile strength reached a maximum value at between 5 and 10 pphr filler loadings. With the exception of stress at 300% extension, all the properties measured decreased at higher filler loadings. Similar effects were also observed with other types of filler particles used in the this work (see Figures 5.17 and 5.18 Section 5.8.2). Similar behaviour has been observed in vulcanisates filled with carbon black (Section 2.1.1). As has already been noted in Chapter Two (Section 2.1.1), Wiegand (39) has suggested that these maxima represent limits to the quantity of filler which can be closely associated with rubber, but in my opinion it is more probable that they merely reflect serious physical interference between neighbouring particles as the filler

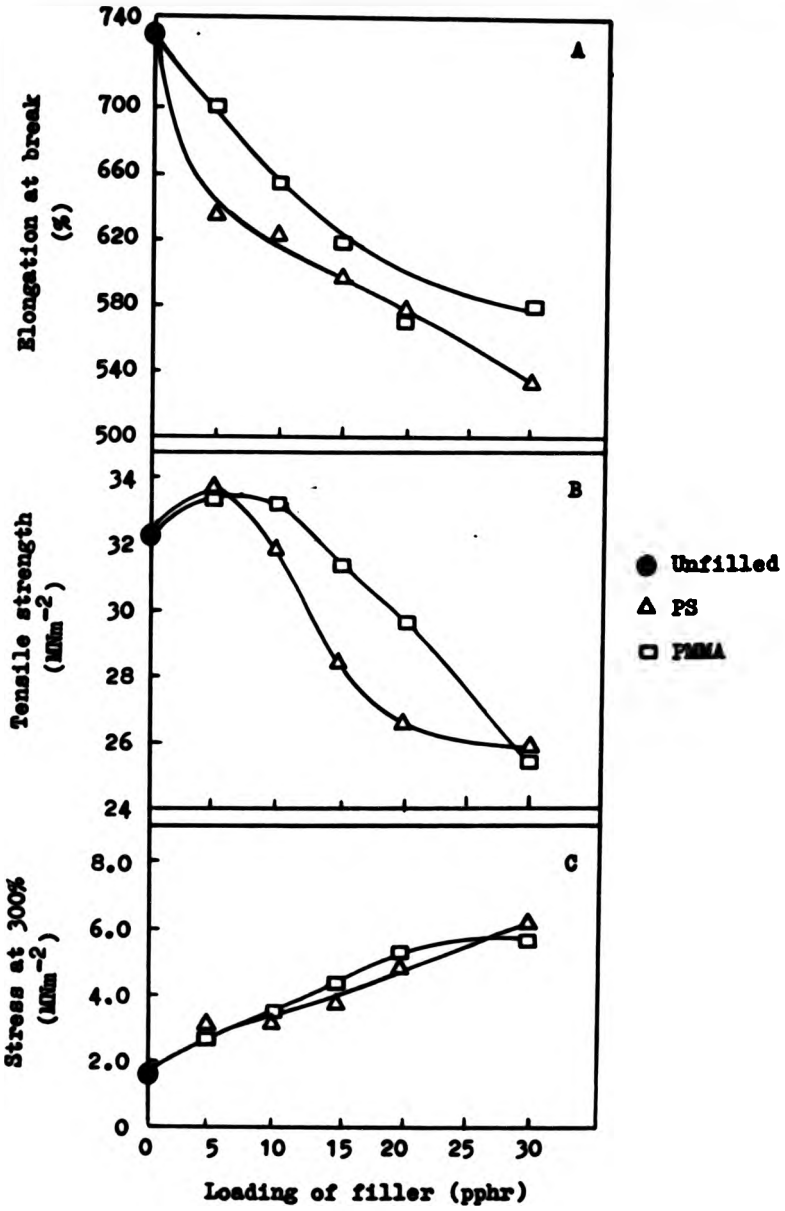


Fig. 5.28 Effect of PS and PMMA particles upon mechanical properties of NR film vulcanisates. Particle sizes: PS - 68nm, PMMA - 69nm

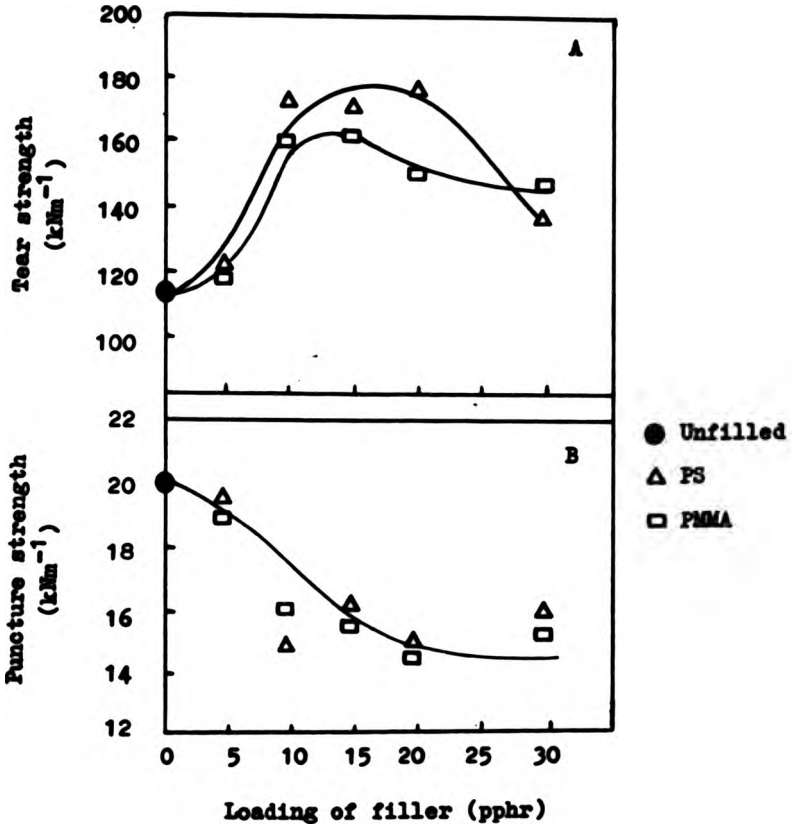


Fig. 5.29 Effect of PS and PMMA particles upon mechanical properties of NR film vulcanisates. Particle sizes: PS - 68nm, PMMA - 69nm

Fig. 5.30 Typical photograph of broken tear test-pieces of filled and unfilled NR latex films. Filler: PS/PDA (90/10) core-shell particles (90/10); particle size - 75nm; figures on the photograph indicate filler loading

concentration becomes sufficiently high. However, in the case of tensile modulus, if a maximum occurs, it is at a higher filler loading than was used in the present work. It may be noted that the distance between neighbouring particles decreases with increasing filler loading. For instance, for latex films containing 5, 10, 20 and 30 pphr of PS particles of size 68nm, the average distances between neighbouring particles are 112, 76, 45 and 31nm respectively.

Of particular interest is the nature of tear propagation at various loadings of these polymeric filler particles. In most cases, the tear proceeded in a stick-slip or knotty manner to leave rough irregular torn surfaces. A typical photograph showing the various types of tearing is shown in Figure 5.30. The effect is more pronounced at 10-20 pphr loadings. This explains why maximum tear strength values were attainable at these loadings, as has been concluded previously in the case of the film vulcanisates which contained overcoated PS particles.

The films obtained from the latex blends which contained 20 pphr or more of some of the fillers often presented problems, such as film cracking, presumably because the filler particles were colloidally unstable towards the coagulant. Such fillers include PS, PMMA and PS particles overcoated with polyallylmethacrylate. However, this problem was not experienced with the particles overcoated with acrylate and methacrylate polymers, polyVeoVa 10 and polyisoprene.

5.14 Results and discussion for measurements of viscosities of blends of rubber and filler latices, and for surface tensions of filler latices

Initially, it was not intended to investigate these properties in the present project. However, because unexpected viscosity changes were observed when the various polymeric filler latices were mixed with NR latex,

some investigation was desirable. In the case of latices such as PBA and PMMA, the viscosities of the blends were approximately as expected, whereas significant viscosity increases were observed when PS and PAcN filler latices were mixed with the rubber latex. Crosslinking the filler particles appears not to alter their behaviour in this respect. However, overcoating the filler particles did reduce significantly the observed increase in viscosity of the blends.

The magnitude of these effects is illustrated in Figure 5.31A which shows typical viscosity changes which were observed when PS/PBA copolymer latices of different copolymer compostions prepared in various ways as outlined in Section 4.2.4 were mixed with NR latex. Generally, regardless of the method of preparation of the copolymer latices, the viscosity of the blends of these copolymer latices with NR latex decreased as the amount of PBA in the copolymers increased. This behaviour appears to be related to the surface tensions of the copolymer latices themselves, the results for which are shown in Figure 5.31B. Similar patterns of viscosity changes were observed with blends of NR latex and latices containing PS particles overcoated with polymers of long-chain acrylates and methacrylates and VeoVa 10 polymers.

Generally, the viscosity changes were found to depend very much upon the surface tensions of the filler latices. It is not known if the viscosities of the blends were significantly time dependent as viscosity measurements were only carried out on the blends of NR and filler latices a day after they had been blended. The viscosity changes during the latex blending can be attributed to incomplete soap coverage of the polymer particles of the filler latices; soap contents tend to be equivalent to a coverage of between 30 and 70% of the total surface area of the particles. Associated with the fact of incomplete soap coverage is the great affinity which these polymers have for added surface-

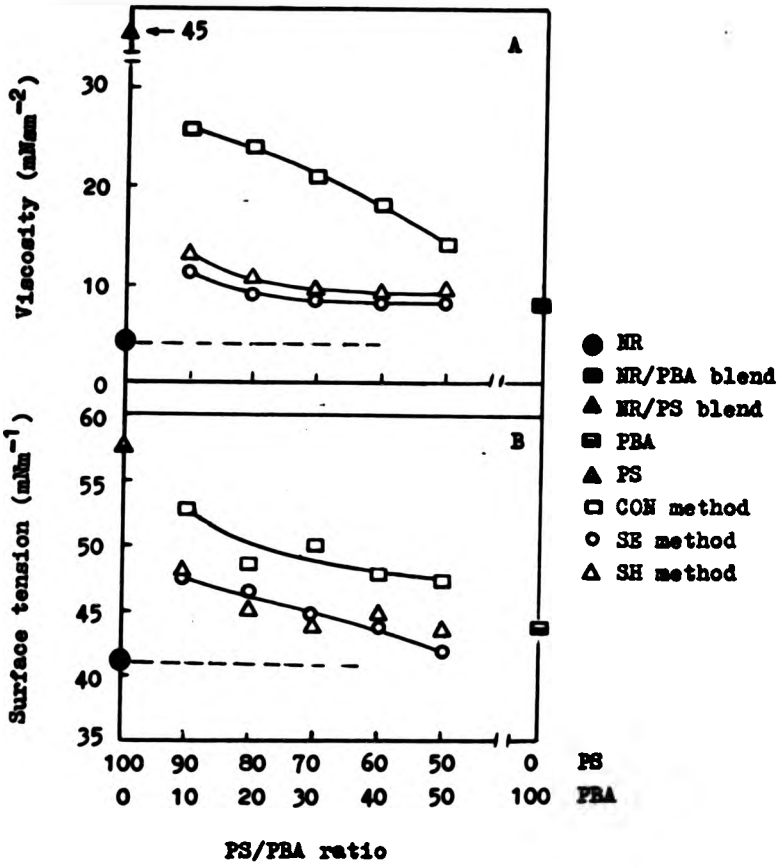


Fig. 5.31 Effect of method of preparation and copolymer compositions of styrene/butylacrylate copolymers upon (A) viscosity of blends of NR (at ca. 26% TSC) and copolymer latices (at ca. 33% TSC) (B) surface tension of copolymer latices. Filler loading in (A): 10 pphr. Particle sizes: as given in Table 5.5

active substances. The tendency is therefore for these polymer latices to rob the otherwise stable NR latex of its stabilisers, and to cause some colloidal destabilisation.

5.15 Effect of milling; comparison of NR vulcanisates containing polymeric filler with NR vulcanisates containing carbon black

The results for the effects of milling and the comparisons between, on the one hand, NR vulcanisates containing rigid polymeric particles and, on the other, NR vulcanisates containing carbon black, are shown in Table 5.12. It can be seen from these results that films prepared directly from NR-polymeric filler latex blends had higher tear strength, and showed knotty tearing, than did the vulcanisate sheets prepared from "milled coagulum" obtained from the blends (see Section 4.4.4 for preparative procedure). The tear strengths for the vulcanisates containing SAF black were inferior to those obtained for the filled latex film, but superior to sheets prepared from the filled latex coagulum which had been milled. The puncture strength values were similar, but the values for the vulcanisates containing carbon black were twice those of NR and polymeric filler latices, and three times the values obtained for the filled films derived directly from the blends of NR and polymeric filler latices.

These results show that milling has a deteriorative effect upon the enhancement of tear strength of NR vulcanisates by added polymer particles, but not upon the other strength properties. In the case of vulcanisates filled with carbon black, it has been argued by Watson et al. (33,40) that the enhancement of tensile modulus results from the chemical attachment of ruptured rubber molcules to carbon black particles, the latter acting as radical acceptors for the ruptured rubber molecules, as has been already noted in Chapter Two (Section 2.1.3A).

Table 5.12 Comparison of NR vulcanisates containing PS and PMMA particles with NR vulcanisates containing carbon black

	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}
Unfilled					
latex film	28.7	833	1.34	106	19.5
latex milled sheet	28.3	763	1.52	37.8	19.1
dry rubber (SMR) sheet	22.7	789	1.72	38.3	16.4
Filled (10pphr)					
PS-filled latex film	30.5	715	2.91	162	15.5
PS-filled milled sheet	31.2	644	3.99	51.4	21.3
PMMA-filled latex film	30.6	745	2.84	165	16.0
PMMA-filled milled sheet	29.3	629	3.63	59.6	22.8
Carbon-black-filled milled sheet (45pphr)	24.3	582	8.64	97.5	20.9

Particle sizes: PS - 68nm, PMMA - 69nm
Carbon black - 20nm
Nature of tearing: only the PS-filled and PMMA-filled latex films showed knotty tearing

Unfortunately, only stress-strain properties of the carbon black-filled vulcanisates were reported by these workers. The mechanism for the shear-induced formation of chemical linkages between rubber and carbon black, with consequent formation of bound rubber suggested by these workers (33) (outlined in Chapter Two (Section 2.1.3.1A), will lead to an increase in the effective crosslink density of the vulcanisate and hence to an increased tensile modulus and possibly also to increased tear strength. A different mechanism must be responsible for the deteriorative effect of milling upon the tear strength of rubber vulcanisates containing polymeric filler particles. However, further investigation of this effect was considered to be outside the scope of the present project. However, it is noted that one probable reason for this effect is that milling destroys the spherical rigid nature of the polymeric filler particles and consequently tears are able to propagate readily without disruption. It may also be that milling has some adverse effect upon the adhesion between the surface of the polymeric filler particles and the rubber matrix in which they were embedded.

It is well-known that the reinforcement of dry rubber vulcanisates is generally achieved by mixing the dry rubber with various types of fine-particle filler, notably the carbon blacks and the colloidal silicas. In the case of articles produced directly from rubber latex films, an analogous process is not available. It is therefore significant that the present investigation has shown that polymeric filler particles introduced by latex blending can reinforce certain mechanical properties, particularly the tear strength, of films obtained directly from NR latex to levels higher than those attainable by mixing with carbon black.

5.16 Further discussion of strength properties of NR film vulcanisates containing various polymeric filler particles

5.16.1 Comparison of tear strength and tensile modulus of film vulcanisates

Evidence has been adduced in the present work that films which were obtained directly from NR latex could be reinforced by polymeric fillers. The emphasis has been upon mechanical properties such as tear strength and puncture strength rather than upon tensile strength and modulus. As remarked before, what is required for some applications is enhancement of tear strength without significant increase in stiffness.

In an attempt to ascertain which of the various polymeric fillers used in the present work will impart optimum tear strength to the rubber films with minimum increase in the stiffness of the vulcanisates, tear strength values were plotted against stresses at 300% extension for the various film vulcanisates. These plots are shown in Figures 5.32 and 5.33. Figure 5.32 shows the relationship between the tear strength and tensile stress at 300% extension for films loaded with 10 pphr of PS particles overcoated with various polymers. The curves in Figure 5.32 were obtained by the following procedure, taking PS/PDA core-shell copolymer particles as an example: Five core-shell latices were prepared in this case, namely PS/PDA (90/10), PS/PDA (80/20), PS/PDA (70/30), PS/PDA (60/40) and PS/PDA (50/50). The average tear strength values (163, 173, 176, 164, and 120 kNm^{-1} respectively, as given in Table 5.6) obtained for the films containing the particles were plotted against the corresponding tensile stress values (2.56, 2.20, 2.24, 2.10 and 1.88 MNm^{-2} respectively). From Figure 5.32, it can be seen that the tear strength reached maximum values when stresses at 300% extension were in the range 2.0 to 2.5 MNm^{-2}, with the exception of vulcanisates

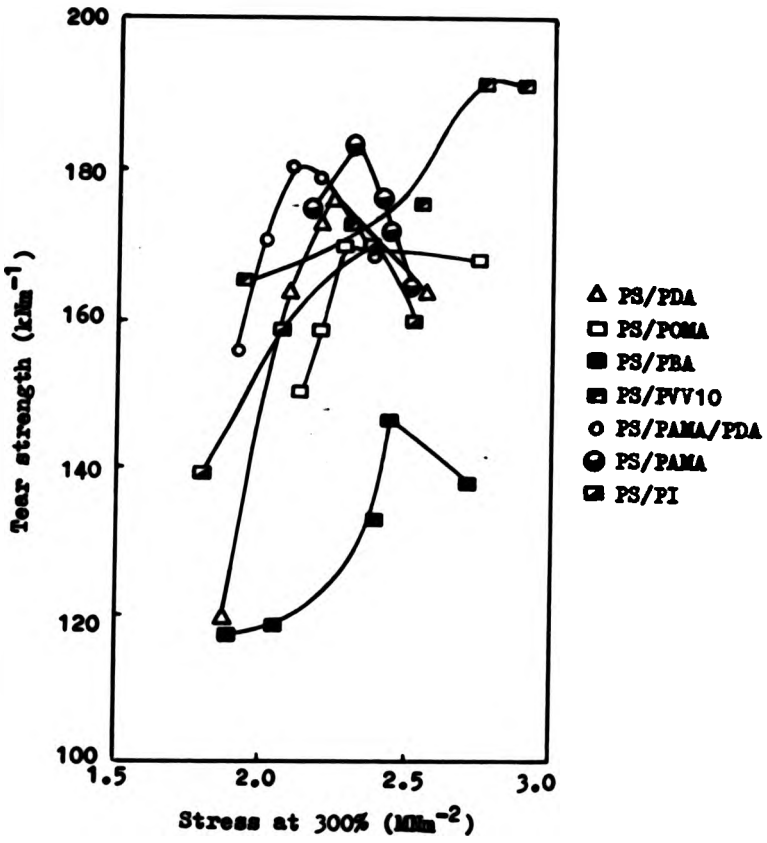


Fig. 5.32 Tear strength vs. stress at 300% extension for NR film vulcanisates containing PS particles overcoated with various polymers. Core/shell ratio is in the range 50/50 to 98/2; filler loading: 10 pphr

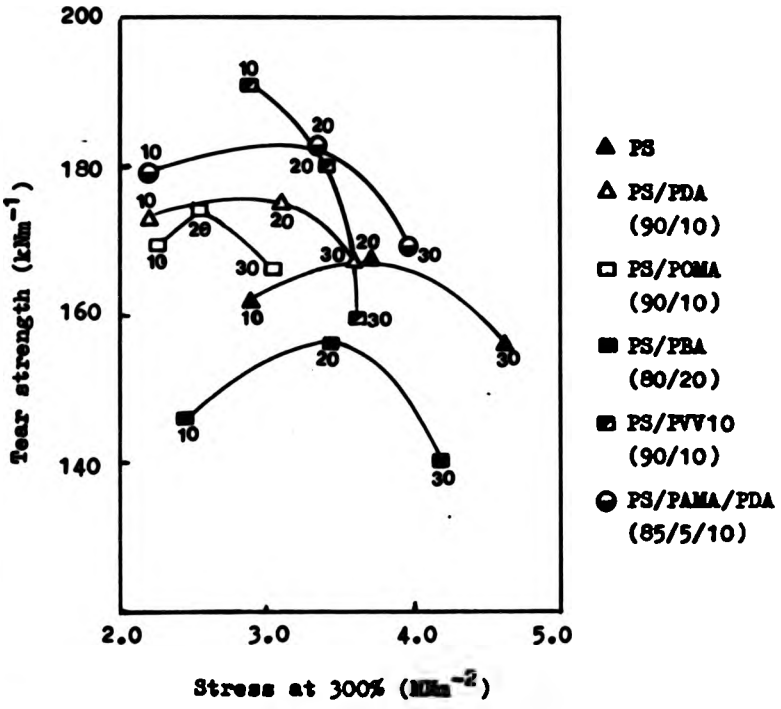


Fig. 5.33 Tear strength vs. stress at 300% extension for NR film vulcanisates containing coated PS particles. Figures appended to points indicate filler loading in pphr. Particle sizes: PS - 68nm, PS/PDA (90/10) - 75nm, PS/POMA (90/10) - 74nm, PS/PBA (80/20) - 69nm, PS/PVV10 (90/10) - 72nm, PS/PAMA/PDA (85/5/10) - 76nm

containing PS particles coated with PVV10.

Figure 5.33 also illustrates the relationship between tear strength and stress at 300% extension for film vulcanisates containing various fillers. The filler particles include: PS particles; and PS/PBA (80/20), PS/PDA (90/10), PS/PAMA/PDA (85/5/10), PS/POMA (90/10), PS/PVV10 (90/10), PS/PI (80/20), PS/PAMA (80/20) core-shell particles. At the indicated copolymer ratios, the various fillers have been found to give optimum enhancement of tear strength. The loadings of these fillers were varied from 10 to 30 pphr, and the tear strength value at each loading was plotted against the corresponding stress at 300% extension. It can be seen that the tear strength of the filled vulcanisates reached optimum values at different stress values, ranging from about 2.50 MNm^{-2} for PS/POMA (90/10) filled vulcanisates to 3.90 MNm^{-2} for PS filled vulcanisates. At higher stresses, and therefore high filler loadings, the tear strength of the vulcanisates decreased.

From the various plots, it can be seen that, even though PS particles overcoated with PVV10 appear to impart optimum tear strength (191 kNm^{-1} at a stress value of 2.77 MNm^{-2}), PS particles overcoated with PDA using allylmethacrylate monomer to bond the PS core covalently to the PDA coat, appear to give reasonably high tear strength (181 kNm^{-1}) at relatively lower stress (2.25 MNm^{-2}). The optimum tear strength value obtained with PS particles overcoated with PAMA falls between the value obtained with these two fillers (i.e., PS/PVV10 (90/10) and PS/PDA (90/10) core-shell particles). By increasing the loadings of the various fillers to between 10 and 30 pphr, the tear strength of the films containing PS/PVV10 (90/10) filler fell sharply with increasing tensile stress, whilst the films loaded with PS/PAMA/PDA (85/5/10) filler showed a steady increase in tear strength with tensile stress up to 20 pphr loading and then decreased. As stated previously, it was not possible to increase the loading of PS/PAMA (80/20) filler above 10 pphr because

of film cracking. From these results, PS/PAMA/PDA core-shell particles appear to confer the best optimum enhancement of tear strength at relatively low tensile stress. As shown in Figure 5.33, films containing uncoated PS particles showed relative low tear strength at relatively high stress. It follows from this that, even though filler rigidity is a necessary prerequisite for the manifestation of reinforcement with respect to modulus and tear strength in rubber vulcanisates, strong adhesion between rubber and filler, resulting from good mixing interaction between the two phases, appear to play the greater role in the enhancement of the tear strength of the film vulcanisates.

5.16.2 Comparison of tear strengths and tensile strengths of film vulcanisates

Figure 5.34 shows the variation of tear strength with tensile strength for film vulcanisates containing 10 pphr of various fillers. The fillers were PS/PDA, PS/POMA PS/PBA, PS/PI and PS/PAMA core-shell copolymer particles of various copolymer compositions ranging from 50/50 to 98/2. The curves in Figure 5.34 were obtained by the following procedure, taking PS/PDA core-shell copolymer particles as an example: Five core-shell latices were prepared in this case, namely PS/PDA (90/10), PS/PDA (80/20), PS/PDA (70/30), PS/PDA (60/40) and PS/PDA (50/50). The average tear strength values (163, 173, 176, 164 and 120 kNm^{-1} respectively, as given in Table 5.6) obtained for the films containing the particles were plotted against the corresponding tensile strength values (31.1, 33.3, 29.0, 29.1 and 25.4 MNm^{-2} respectively). Generally, the tear strength values increased rapidly with increasing tensile strength, the rate of increase becoming progressively less rapid.

Figures 5.35 also shows the relationship between tear strength and tensile strength for film vulcanisates containing 10-30 pphr of various core-shell copolymer

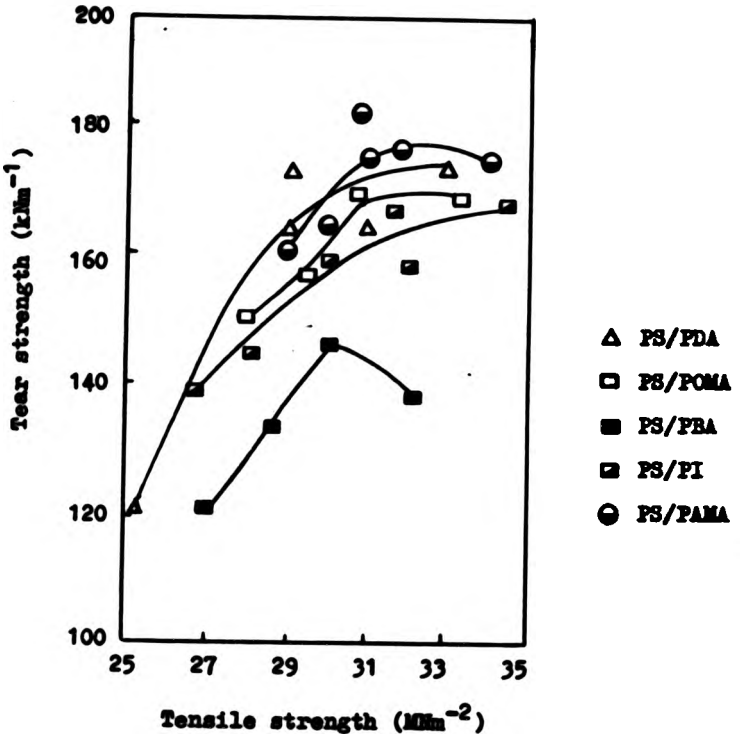


Fig. 5.34 Tear strength vs. tensile strength for NR film vulcanisates containing PS particles overcoated with various polymers. Core/shell ratio is in range 50/50 to 98/2

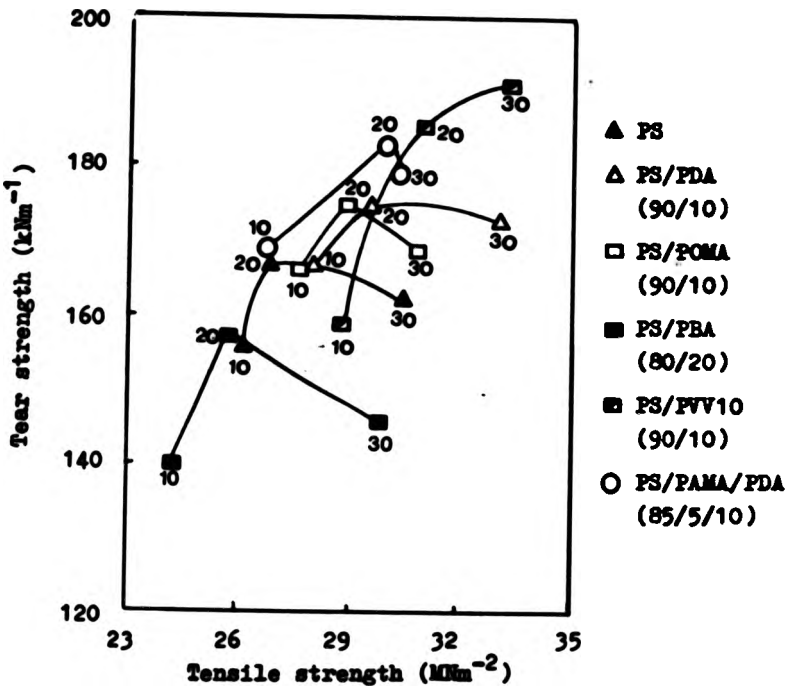


Fig. 5.35 Tear strength vs. tensile strength for NR film vulcanisates containing coated PS particles. Figures appended to points indicate filler loading in pphr. Particles sizes: PS - 68nm, PS/PDA (90/10) - 75nm, PS/POMA (90/10) - 74nm, PS/PBA (80/20) - 69nm, PS/PVV10 (90/10) - 72nm, PS/PAMA/PDA (85/5/10) - 76nm

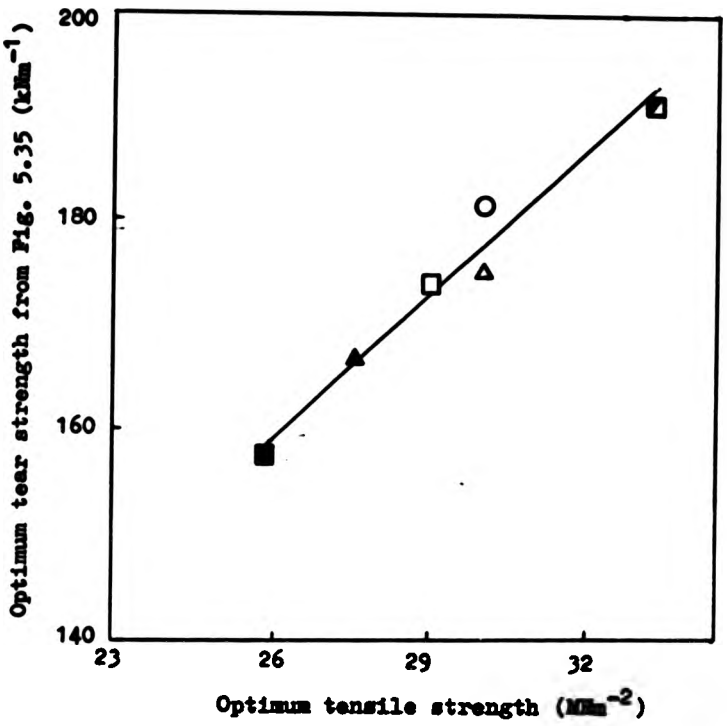


Fig. 5.36 Comparison of optimum tear strength values obtained from Fig. 5.35 and corresponding optimum tensile strength values for NR film vulcanisates containing PS particles overcoated with various polymers. ▲ PS - 68nm, ■ PS/PBA (80/20) - 69nm, □ PS/PCMA (90/10)-74nm, △ PS/PDA (90/10) - 75nm, ○ PS/PAMA/PDA (85/5/10) - 76nm, ▣ PS/PVV10 (90/10) - 72nm

particles. The curves obtained for the films containing other core-shell particles have been omitted from this diagram for clarity. From the various plots, with the exception of that for the films containing PS/PVV10 (90/10), it can be seen that the tear strength reached optimum values at different values of tensile strength for each filler, and then decreased. These maxima correspond to a filler loading of approximately 20 pphr in all cases and are as follows in increasing order for the various core-shell copolymer particles: PS/PBA (80/20), PS/POMA (90/10), PS/PDA (90/10), PS/PAMA/PDA (85/5/10) and PS/PVV10 (90/10) core-shell copolymer particles. The tensile strength values, as shown in Figure 5.35, appear to increase in the same order. This shows that for these materials, the tear strength increases with increasing tensile strength. These results and also those shown in Figure 5.34 suggest that there is a relationship between optimum tear strength and optimum tensile strength. In Figure 5.36, the optimum tear strength values obtained from the various curves shown in Figure 5.35 were plotted against the corresponding optimum tensile strength values for each vulcanisate. The relationship was found to be linear to a remarkable degree of accuracy. A relationship of this type would be expected if there is good adhesion between the filler and the rubber matrix, because at moderate filler loadings such adhesion would be expected to give optimum tear strength and optimum tensile strength in the system under investigation here. The basis of the observed relationship can be interpreted in the light of the previously stated relationship between tear energy ,T, and the work per unit volume, e, in simple extension (Equation 5.1)

$$T = ed$$

where d is the effective diameter at the tip of the tear. From this equation and the observed linear relationship between tear strength and tensile strength shown in Figure 5.36, it is concluded that failures at the filler-rubber

interface should not occur until high stresses are reached. It follows from these results that, as has been concluded in Section 5.9, reinforcing fillers must have good adhesion to the rubber matrix; furthermore, the better the adhesion, the higher the stress at which failure will take place and therefore the higher the tear strength. This explain why, for instance, vulcanisates containing PS particles and PS/PBA core-shell particles have relatively lower tear strengths, as shown in Figure

Table 5.13 Prediction of tear strength values from tensile strength values for films from NR latex containing 20 pphr of filler particles using equation 5.2

Filler	Tensile strength MNm^{-2}	Tear strength (kNm^{-1})	
		Experimental value	Value predicted by equation 5.2
PS	26.9	167	163
PS/PBA (80/20)	25.9	156	158
PS/PDA (90/10)	29.6	175	176
PS/PAMA/PDA (85/5/10)	30.1	183	178
PS/POMA (90/10)	28.5	174	170
PS/PVV10 (80/20)	31.0	180	182
PS/PI (80/20)	28.8	173	158
PS/PAMA * (80/20)	25.9	146	158

* Films containing these particles were not homogeneous because the films cracked on drying.

5.36, this being attributable to the absence of strong adhesion between the particles and the rubber matrix. PS particles appear to give higher tear strength than PS/PBA core-shell particles because of their high rigidity, as rigidity has been shown (see Section 5.6) also to play an important role in the absence of strong rubber-filler adhesion.

The equation for the linear regression of tear strength (T) upon tensile strength (σ) for the data given in Figure 5.36 has been calculated to be

$$\frac{T}{kNm^{-1}} = 40.8 + 4.55\frac{\sigma}{MNm^{-2}} \qquad 5.2$$

When this empirical equation was used to estimate the expected optimum tear strength for the various vulcanisates containing overcoated PS particles, the predicted values, given in Table 5.13 agree well with the experimental values.

5.16.3 Application of some equations which have been proposed to describe effect of filler loading upon tensile modulus

Several attempts have been made to derive formulae giving modulus of an elastomer containing dispersed particles relative to that of the elastomer matrix. However, as far as is known, no similar attempts have been made in the case of tear strength and tensile strength. The Young's moduli of the various filled vulcanisates investigated in the present work were not determined. However, several of these equations have been used to represent the tensile stress at 100% extension of NR film vulcanisates containing various filler particles. Some of these equations are illustrated in Figure 5.38. The equations (discussed in Chapter 2 Section 2.2.1) that have been used include :

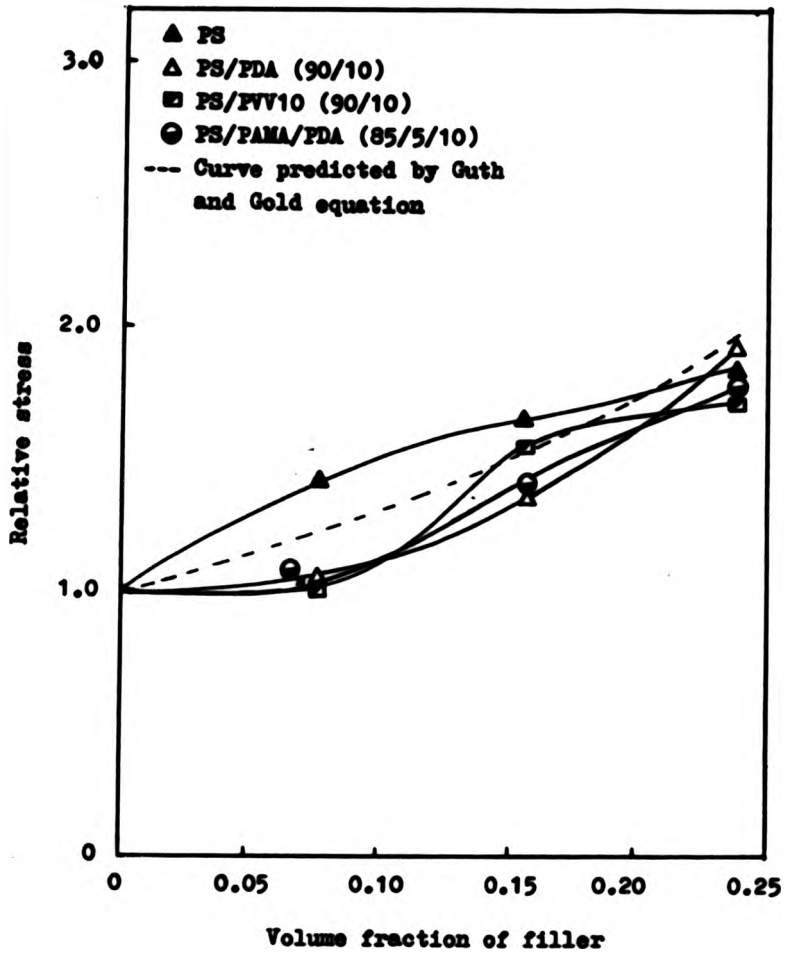


Fig. 5.37 Relative stress at 100% extension as a function of filler loading for NR film vulcanisates, together with prediction given by Guth and Gold equation. Particle sizes: PS - 68nm, PS/PDA (90/10) - 75nm, PS/PVV10 (90/10) - 72nm, PS/PAMA/PDA (85/5/10) - 76nm

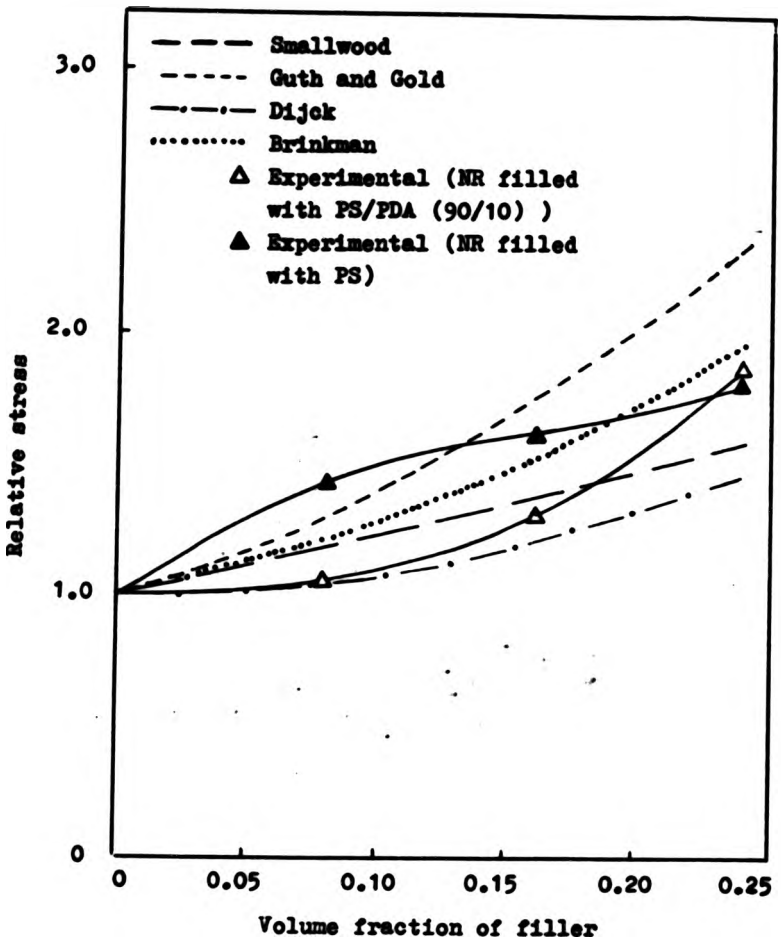


Fig. 5.38 Relative stress at 100% extension as a function of filler loading as predicted by various equations. Particle sizes: PS - 68nm, PS/PDA (90/10) - 75nm

the Smallwood equation (2.1)

$$E = E_1(1 + 2.5C_2)$$

the Guth and Gold equation (2.2)

$$E = E_1(1 + 2.5C_2 + 14.1C_2^2)$$

the Djick equation (2.4)

$$E = E_1\left[1 + \frac{1.25C_2}{1 - 1.28C_2}\right]$$

the Brinkman equation

$$E = E_1(1 - C_2)^{-5/2}$$

Figures 5.37 and 5.38 show relative stress as function of filler loading together with predictions given by various equations. From these graphs, it is clear that there are deviations between experimental data and the various theoretical prediction (Figure 5.38), and also between the predictions given by the various equations (Figure 5.38). This was not unexpected because factors influencing reinforcement, such as filler particle nature, particle structure and particle surface amongst others, are inter-related. For this reason, it is unlikely to be easy to devise a formula which will take all the factors into account. It is evident from the results obtained in the present investigation that this is so. Most of these equations have originated from the effect of dispersed particles upon viscosity. Rutgers (41) in his review lists some 200 different equations which have been proposed over the years for relating the viscosity of suspension to particle concentration. Rutgers commented that, although these equations often originated for some special disperse system, they have been applied theoretically or empirically to a whole range of systems. The same function

has been used for a variety of systems, such as rigid sphere suspensions, emulsions, suspensions of non-spherical particles, polymer solutions and structured systems with linking forces between the particles.

Generally, the discrepancy between experimental data and theoretical prediction is often explained by invoking the existence of additional effective crosslinks arising from filler-elastomer bonds. This view was held by Sheik (42), in his Thesis. He applied some of these equations to the Young's moduli of elastomers filled with glass beads, and found that there were discrepancies between the observed modulus and the theoretical predictions, even at small filler loading. He attributed the discrepancies to additional crosslinks due to filler-matrix bonding. However, from the values of tensile stress obtained for films fron NR latex containing various core-shell copolymer particles in the present work, the discrepancy between the experimental data and the theoretical prediction cannot be entirely ascribed to the adhesion between filler and rubber. In fact, it has been found in the present work that strong adhesion between filler and rubber is not a necessary prerequisite for the manifestation of enhancement of tensile stress. For instance, uncoated PS particles were found to impart greater enhancement of tensile stress than did the PS particles overcoated with polymers of long-chain acrylates and methacrylates, despite the fact that there was almost certainly better adhesion between the rubber and coated particles than between the rubber and the uncoated particles.

In conclusion, it can be said that the poor predictions given by these equations, together with the various factors that have been found to influence the mechanical reinforcement of films from NR latex in the present work, indicate that unselective use of these equations is no more than a mathematical exercise.

5.17 Discussions of other observations relating to blends of NR and filler latices

It was observed that films from the blends of NR and filler latices dried down rather more slowly than did films from unfilled NR latex. This is attributed to the higher soap content of the the films from the blends which caused the deposits to be somewhat hygroscopic during the latter stages of drying.

Of particular interest is the appearance of the films produced when these latices were dried. Whereas the unfilled NR latex formed coherent films, the blends of NR and filler latices gave cracked films when the filler concentration exceeded 20 pphr, particularly with filler latices which contained uncoated particles. This may have been a consequence of colloidal instability of the contained filler particles towards the coagulant used for the dipping process. Similarly, when the latices were coagulated by the addition of acid, the filled latices formed a fine precipitate, especially at high (> 10 pphr) filler concentration, whilst the unfilled latex formed a compact coagulum.

CHAPTER SIX : RESULTS AND DISCUSSION OF BEHAVIOUR OF POLYMERIC FILLERS IN FILMS DERIVED FROM OTHER LATICES

6.1 Introduction

Experiments were carried out with prevulcanised NR latex, styrene-butadiene rubber (SBR) latex and acrylonitrile-butadiene rubber (NBR) latex. The filler particles which were used in these experiments included polystyrene particles overcoated with polydodecylacrylate, polyVeoVa 10 and polyallylmethacrylate. All the core-shell polymers were prepared by the shot-growth method. These particles were expected to give optimum reinforcement on the basis of the principles which emerged from the experiments on post-vulcanised NR latex films. However, in the case of NBR latex, this is not necessarily the case because the filler particle coating may not mix very well with the rubber matrix. A number of experiments were carried out with prevulcanised NR latex, but only a few experiments were carried out with SBR and NBR latices in the present work. No significant reinforcement of the tear strength and puncture strength of the films derived from these latices was achieved, as the results reported in the present Chapter will show.

6.2 Effect of polymeric filler particles upon mechanical properties of films from prevulcanised NR latex

6.2.1 Preliminary experiments with prevulcanised NR latex supplied by London Rubber Company

The behaviour of the following filler particles were investigated: (I) polystyrene particles; (II) polystyrene particles overcoated with polyVeoVa 10 (PS/PVV10 (90/10)) and polydodecylacrylate (PS/PDA (90/10)); (III) polystyrene overcoated with polydodecylacrylate using

Table 6.1 Effect of 10 pphr polymeric filler particles upon mechanical properties of films from prevucanised NR latex (supplied by LRC)

Filler	Particle size nm	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}
None	-	22.6	785	1.75	116	16.4
PS	72	21.0	660	2.59	110	16.0
PS/PDA (90/10)	75	19.2	646	2.67	103	15.3
PS/PAMA/PDA (85/5/10)	76	19.8	643	2.80	104	16.7
PS/PVV10 (90/10)	72	19.0	646	2.59	110	15.2
PS/PAMA (80/20)	75	19.5	660	2.65	120	16.8

All the films were dried at 100°C for 30 minutes

Nature of tearing: all the films (filled and unfilled) showed knotty tearing

polyallylmethacrylate as a linker (PS/PAMA/PDA (85/5/10)); (IV) polystyrene particles whose surfaces were functionalised with allylmethacrylate units (PS/PAMA (80/20)).

The prevulcanised latex was further compounded by adding sulphur (0.5 pphr), zinc stearate (1.25 pphr) and antioxidant 2246 (0.25 pphr). The compound formulation for the original prevulcanised latex was not disclosed. The optimum drying/curing time for the latex films was found to be 30 minutes at 100°C.

Table 6.1 gives the effect of the various fillers upon the mechanical properties of the films from the prevulcanised latex. It can be seen that, even though the filler particles appear to increase the tensile stress at 300% extension and decrease the elongation at break, all other properties, particularly tear strength, appear not to be affected. In fact, it appears that the effect of the fillers was to slightly reduce the tear strength.

6.2.2 Experiments with prevulcanised NR latex prepared in the laboratory

As a result of the disappointing results obtained with prevulcanised NR latex supplied by London Rubber Company, it was decided to prevulcanise NR latex for various periods of time ranging from 0.5 to 6 hours at 60°C as outlind in Section 4.4.3. The blends of the rubber and filler latices were prepared in two ways: (I) by blending the prevulcanised latex with the filler latex and (II) by blending the rubber latex with the filler latex and then prevulcanising the blend. Films obtained from these blends are designated as Type I and Type II respectively. The films derived from the latex blends were dried for 24 hours at room temperature (ca. 20°C) and then heated for 30 minutes at 100°C.

Table 6.2 gives the mechanical properties of the film vulcanisates containing PS/PVV10 (90/10) core-shell copolymer particles. It can be seen that there is

Table 6.2 Effect of 10 pphr of PS/PVV10 (90/10) core-shell particles upon mechanical properties of films from prevulcanised NR

Time of prevulcanisation hr	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}
	unfilled film: dried at 100°C for 30 mins				
0	28.5	824	1.36	118	17.3
1/4	29.8	771	1.85	127	18.5
1/2	30.0	760	1.95	137	17.5
1	28.0	746	1.86	142	16.8
3	25.0	661	2.17	121	17.7
5	23.6	660	2.23	111	18.5
6	23.5	646	2.34	112	19.7
	unfilled film: dried at 22°C for 24 hrs				
1	25.9	660	1.86	140	18.8
	filled film: Type I, dried at 100°C for 30 mins				
1	23.2	640	2.67	127	15.6
3	18.1	546	3.36	90.3	16.3
5	17.6	545	3.51	92.3	16.0
6	14.7	556	3.94	77.8	16.1
	filled film: Type II, dried at 100°C for 30 mins				
1	23.9	700	2.55	117	15.6
3	20.2	598	3.08	100	16.3
6	19.6	578	3.53	85.6	16.3
	filled film: Type II, dried at 22°C for 30 mins				
1	22.4	648	2.72	115	18.1
3	19.3	589	3.19	101	16.5
6	16.7	548	3.50	76.1	16.4

Particle size : 72nm

Nature of tearing: all the films showed knotty tearing

no significant difference between the mechanical properties of the films derived from Type I and from Type II latex blends. In both cases, the filler particles increased the tensile stress at 300% extension and decreased the elongation at break of the film vulcanisates. The filler particles did not enhance the other strength properties; in fact, they appear to decrease the tensile strength and tear strength of films derived from the latices prevulcanised for long period of time. There were no significant differences between the properties of the films dried at room temperature and at 100°C.

6.2.3 Summary of behaviour of polymeric filler particles in prevulcanised latex films, and comparison with post-vulcanised latex films

Table 6.3 summarises the effects of added polymer particles upon mechanical properties of prevulcanised and post-vulcanised NR latex films. It can be seen that the filler particles did not improve the tear strength of the prevulcanised latex films. In both cases, stress at 300% extension increased, elongation at break decreased, and there was no significant change in the puncture strength. The particles appear to decrease the tensile strength of the prevulcanised latex film vulcanisates while their presence in the post-vulcanised latex film vulcanisates did not change the tensile strength significantly.

Of particular interest is the nature of the tear propagation of the filled films. The tear of the filled post-vulcanised films and the filled prevulcanised films proceeded in a knotty manner but the degree of knottiness (as assessed by visual observation) was more pronounced with the filled post-vulcanised films. It was expected that, since the tearing of the filled prevulcanised latex films proceeded in a knotty manner to some extent, the tear strength would be similar to that of the post-vulcanised latex films. This was not the case, as is

Table 6.3 Effect of 10 pphr of filler particles upon mechanical properties of films from unvulcanised NR latex and prevulcanised NR latex

Vulcanisate	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Puncture strength kNm^{-1}
Unfilled					
post-NR	28.5	824	1.36	118	17.3
pre-NR(LAB)	28.0	746	1.86	142	16.8
pre-NR(LRC)	22.6	785	1.75	116	16.4
Filler:PS/PAMA (80/20)					
post-NR	30.2	776	2.49	177	17.3
pre-NR(LAB)					
Type I	24.7	652	2.79	142	17.3
Type II	23.2	620	3.31	117	16.1
pre-NR(LRC)	19.5	660	2.65	120	16.8
Filler:PS/PVV10 (90/10)					
post-NR	32.5	785	2.48	187	14.9
pre-NR(LAB)					
Type I	23.2	640	2.67	127	16.0
Type II	23.9	700	2.55	117	15.6
pre-NR(LRC)	19.0	646	2.59	110	15.2

All the films were dried at 100°C for 30 mins

post-NR: films from NR latex
pre-NR(LAB): films from latex prevulcanised in the laboratory for 1 hour
pre-NR(LRC): films from prevulcanised NR latex supplied by London Rubber Company

Particle sizes: PS/PAMA (80/20) - 75nm
PS/PVV10 (90/10) - 72nm

evident from Table 6.3. In fact, tearing of the films from the unfilled prevulcanised latex also proceeded in a knotty manner unlike that of post-vulcanised films which proceeded smoothly leaving smooth torn surfaces. This indicates that the nature of the tear propagation in the prevulcanised latex films was not a consequence of the presence of the filler particles,

As already stated in Chapter One (Section 1.3), it was known before the commencement of the project that the tear strength and puncture strength of rubber films can be increased by adding minor amounts of various rigid spherical polymer particles, in the form of aqueous latices, to the NR latex from which the films are made. This was evident from, for example, the paper by Gorton (1). This has been confirmed in the present work, particularly with the use of core-shell polymer particles. However, attempts have been made by other workers (2) to use polymer particles at levels in the range 10-30 pphr to improve the tear strength and puncture strength of film from prevulcanised NR latex. No significant improvements in these properties have been observed. This is in complete agreement with the results obtained for films from filled prevulcanised latex in the present work. These earlier workers did not give any reason for the differences in the behaviour of the polymer particles in the films derived from post-vulcanised NR latices on the one hand, and from prevulcanised NR latices on the other. A possible explanation for the differences can be offered. Evidence has been adduced in the previous Chapters that enhancement of tear strength by filler particles is mainly a consequence of adhesion between the filler and the rubber matrix in which they are embedded, and that high tear strength values are attainable at relatively low modulus when there is good adhesion between the rubber and the filler. It is unlikely that the inability of the filler particles to reinforce films from prevulcanised latex is due to weak rubber-filler adhesion. In fact, the adhesion between the PS/PAMA particles and the rubber

matrix would be expected to be good because co-vulcanisation should have occurred during the 30 minutes heating at 100°C. This period of heating should have provided opportunity for further vulcanisation, and for the re-arrangement of sulphur crosslinks already present. A more likely explanation of the failure of the particles to reinforce films from prevulcanised NR latex is that the rubber matrix of these films is inherently weak because of poor interparticle coalescence. Also, the filler particles were much smaller than the particles in the prevulcanised NR latex, so that the final films comprised large rubber particles incompletely coalesced, interspersed with much smaller rigid filler particles. The results obtained in the present investigation suggest that, in all cases investigated, the tearing of the prevulcanised films occurred by failure at the interface between the rubber particles, and that the presence of filler particles had little effect upon the process.

6.3 Behaviour of polymeric filler particles in styrene-butadiene rubber and acrylonitrile-butadiene rubber latices

Initially, it was intended to carry out detailed investigations of the reinforcement of SBR and NBR latices utilising the principles which emerged from the experiments on post-vulcanised NR latex films. However, unfortunately only limited time was available for these investigations. For this reason, only very superficial investigations have been possible, and further experiments will be required, as suggested in Section 7.3, before any definite conclusion can be drawn.

6.3.1 Determination of optimum cure for films from styrene-butadiene rubber and acrylonitrile-butadiene rubber latices

The latex films were prepared as outlined in Section

Table 6.4 Effect of time of cure upon the mechanical properties of films derived from SBR and NBR latices

Cure min	Film	Tensile strength MNm^{-2}	Elongation at break %	Stress at 100% MNm^{-2}	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Nature of tear
15	SBR	16.3	547	1.27	2.11	24.2	N
	NBR	-	-	-	-	-	-
30	SBR	19.0	440	1.63	3.33	24.5	N
	NBR	23.2	496	-	5.18	26.2	N
60	SBR	13.5	325	1.65	3.73	24.3	N
	NBR	15.9	438	-	5.78	29.2	N
90	SBR	13.4	323	1.67	4.40	22.3	N

Table 6.5 Effect of 10 pphr of PS/PVV10 (90/10) core-shell particles upon mechanical properties of films from NR, SBR and NBR latices

Film	Tensile strength MNm^{-2}	Elongation at break %	Stress at 300% MNm^{-2}	Tear strength kNm^{-1}	Nature of tear
Unfilled					
NR	28.7	833	1.34	106	N
SBR	19.0	440	3.33	24.5	N
NBR	23.2	496	5.18	29.2	N
Filled					
NR	34.2	731	2.92	191	K
SBR	16.2	510	4.60	27.3	N
NBR	22.9	483	5.60	33.0	N

Particle sizes: 72nm
K - knotty, N - not knotty

4.4.2. They were vulcanised at 100°C for various periods of time ranging from 15 to 90 minutes. The mechanical properties of the films obtained from the rubber latices are given in Table 6.4, from which it can be seen that the various mechanical properties reached maximum values at different cure times. However, unlike NR latex film vulcanisates, the effect of cure upon the tear strength values of these vulcanisates is not significant. For the purpose of the present investigation, an optimum cure of 30 minutes was assumed.

6.3.2 Effect of polymeric filler particles upon mechanical properties of films from styrene-butadiene rubber and acrylonitrile-butadiene rubber latices

The effects of PS particles overcoated with PVV10 upon the mechanical properties of films from SBR and NBR latices at 10 pphr loading are given in Table 6.5. The properties of NR film vulcanisates at the same loading are also given for comparison. It is clear from these results that the filler particles did not reinforce the mechanical properties of the films derived from the synthetic rubber latices. The reason may be that strong adhesion between the filler particles and the rubber matrix necessary for the manifestation of reinforcement, particularly for enhancement of tear strength, is lacking in the filled films. Evidence for the absence of strong adhesion between filler particles and the sythentic rubber matrix comes from a comparison of scanning elctron micrographs of films derived from NR, SBR, and NBR latices containing PS/PVV10 (90/10) core-shell polymer particles. Figure 6.1 shows a selection of scanning electron micrographs of films cast from the filled rubber latices. While the filler particles appear to be completely buried in the rubber matrix in the case of NR film vulcanisates, they can be seen as loose particles in the case of SBR and NBR film vulcanisates.

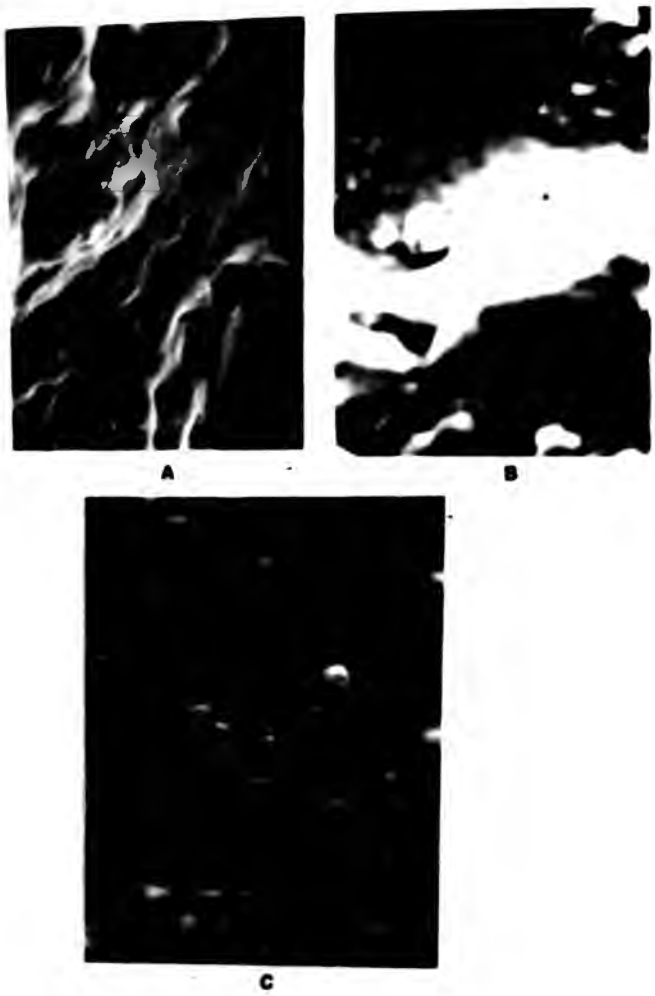


Fig. 6.1 Scanning electron micrographs of ruptured surfaces of tensile test-pieces of various rubber films containing 10 pphr of PS/PVV10 (90/10) filler (72nm). (A) NR; (B) SBR; (C) NBR; magnification X 5,000

CHAPTER SEVEN : CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 Introduction

Various factors and filler characteristics which influence the ability of added polymer particles prepared as latices by emulsion polymerisation to reinforce the mechanical properties of films derived from rubber latices have been investigated. In particular, the investigation has been concerned with the following:

I) the factors which influence the ability of added polymer particles to reinforce the mechanical properties of post-vulcanised NR latex films;

II) the behaviour of polymer particles in latex films derived from other latices, such as prevulcanised NR latex, styrene-butadiene rubber latex and acrylonitrile-butadiene rubber latex, using particles which were expected to give optimum reinforcement on the basis of the principles which had emerged from the experiments on post-vulcanised NR latex films.

A range of filler latices has been prepared and blended with NR latex. Films have been obtained by coagulant dipping and then vulcanised. Electron micrographs have shown excellent dispersion of the individual filler particles in the rubber matrix. The mechanical properties of the latex films have been determined. The emphasis has been upon the enhancement of mechanical properties such as tear strength, rather than tensile strength and modulus. In fact, the objective had been to keep the modulus as low as possible.

The concluding of this thesis will deal with two remaining matters: (a) it reviews the progress which has been made towards attaining the stated objectives of this

investigation; and (b) it gives suggestions for further work that are thought to be appropriate for the continuation of this investigation.

7.2 Factors and filler characteristics which influence reinforcement of post-vulcanised natural rubber latex films

7.2.1 Effect of particle size of filler

Measurements of mechanical properties of NR latex films containing polystyrene latex particles have confirmed that small particle size is a necessary prerequisite for the manifestation of optimum enhancement of strength properties in rubber vulcanisates. For each type of filler particle, tear strength, tensile strength and tensile stress at 300% extension were found to decrease linearly with increasing particle size of filler, whilst elongation at break and puncture strength increased approximately linearly with increasing particle size. There was no significant difference between the mechanical properties of films containing filler particles of large size (ca. 500nm) and the unfilled films. Both polystyrene and polymethylmethacrylate fillers appear to have similar reinforcing effects upon the rubber, indicating that polarity is not an important factor in the mechanical reinforcement of films derived from rubber latices by rigid polymer particles.

The reason for the enhancement of strength properties by the small particle size in both fillers is not entirely clear. It can probably be ascribed to the increase in interfacial area per unit volume as particle size decreased and to stress concentration brought about by the presence of small particles. As particle size decreases, agglomeration of particles tends to increase with corresponding decrease in maximum packing volume. This effect will be expected to increase tensile stress.

7.2.2 Effect of rigidity of filler

Three groups of filler particles, (i) polyacenaphthylene particles, (ii) polystyrene and polymethylmethacrylate particles, (iii) polybutylacrylate particles, in order of decreasing rigidity, have been used for the study of the effects of rigidity of filler particles upon the reinforcement of films from natural rubber latex. They have different T_g values as follows: (i) >250°C, (ii) 105-100°C and (iii) -57°C respectively. It appears that the three groups reinforce in different ways, and that the reinforcing abilities of the fillers are directly related to the rigidity of the particles.

The tensile stress at 300% extension and the tear strength of the film vulcanisates were found to increase with the rigidity of the contained filler particles, whereas the elongation at break decreased. No direct relationship was found between the other strength properties and the rigidity of the contained particles. It was found that, with the exception of the film containing polybutylacrylate particles, tearing of the film vulcanisates proceeded in a knotty manner to leave rough irregular torn surfaces, thereby increasing the tear strength of the rubber films. In the case of the film vulcanisates containing polybutylacrylate particles tearing proceeded smoothly and produced smooth torn surfaces in the same way as the unfilled rubber films. The stress-relaxation behaviour of the film vulcanisates indicates that the presence of the rigid particles in the rubber matrix creates a hydrodynamic disturbance which is accompanied by lengthening of the relaxation time-spectrum of the film vulcanisates.

7.2.3 Effect of crosslinking polymeric filler particles

The effect of crosslinking the polymer molecules within polystyrene particles and polymethylmethacrylate particles upon abilities to reinforce have been studied.

Crosslinking these filler particles appears not to affect their ability to enhance tear strength significantly. However, the puncture strength showed slight improvement. The elongation at break decreased, and tensile stress at 300% extension increased with increasing degree of crosslinking. The film forming behaviour of the rubber latex containing the crosslinked particles was not as good as that of rubber latex containing particles that were not crosslinked. This may have contributed to the absence of any further enhancement of tear strength of the films from natural rubber latex by crosslinking the particles.

7.2.4 Effect of promoting interaction between polymeric filler particles and rubber matrix

Polystyrene particles have been used for this investigation. The interaction between the surface of the particles and the rubber matrix has been promoted by providing the particles with a surface which tends to mix with the rubber matrix, and also with a surface which is expected to react chemically with the rubber matrix. The mixing interaction has been achieved by overcoating the polystyrene particles with polyVeoVa 10, and with polymers of long-chain acrylate/methacrylates, such as dodecyl-acrylate, dodecylmethacrylate and octadecylmethacrylate by shot-growth emulsion polymerisation. Measurements of particle size and surface tension have shown that the polystyrene particles were probably completely overcoated with the coating polymers. The chemical interaction has been promoted by functionalising the surface of the polystyrene particles with allylmethacrylate and with isoprene units. The presence of unreacted double bonds in the copolymers contained in the resulting latices was confirmed by measurement of unsaturation using Wijs' method.

Generally, the strength properties of the films containing the polystyrene particles overcoated with polyVeoVa 10 and a range of acrylate polymers were found

to vary with the copolymer compositions, decreasing at high content (over 30%) of the coating polymer in the copolymer. Overcoating the polystyrene particles with thin layers of the coating polymer was found to enhance the ability of the particles to reinforce the tear strength of films from natural rubber latex. In most cases, maximum tear strengths were attained when the core-shell particles embedded in the rubber matrix contained 10-20% of the coating polymer. Tearing proceeded in a knotty manner to leave rough irregular torn surfaces. Of the various particles overcoated with polymers of long-chain acrylate/methacrylates and VeoVa 10 polymer, particles overcoated with polydodecylacrylate and polyVeoVa 10 were found to give better enhanced tear strength and tensile strength. The latter coated particles were found to give higher tear strength and tensile strength at relatively higher stress at 300% extension; while the former were found to give better enhanced puncture strength, particularly when polystyrene/polydodecylacrylate (90/10) core-shell particles were used. The possibility of enhancing still further the level of reinforcement imparted by the overcoated polystyrene particles has been investigated by attempting to bond the coating polymer (polydodecylacrylate) covalently to the surface of the polystyrene particles using allylmethacrylate as a bonding monomer. Core-shell particles of this type appear to give higher tear strength values than do the polystyrene/polydodecylacrylate core-shell particles without a bonding monomer, there being no appreciable increase in the other strength properties. However, the differences in the tear strength values are insufficiently significant to justify the use of a bonding monomer.

The enhancement of tear strength and tensile strength by the various overcoated polystyrene particles is attributed to the improved adhesion between the filler and the rubber matrix in which they were embedded. The enhancement of these strength properties by the core-shell particles can be explained by assuming that under stress

the core-shell particles yield and absorb energy, thus delaying the onset of crack propagation. Energy dissipation is assisted by the efficient transmission of the applied stress through the elastic shells which are bonded to the rigid core-particles, as well as by the presence of phase mixing at the interface between core-shell particles and rubber phase. Scanning electron micrographs of the ruptured surfaces of tensile test-pieces have confirmed differences in adhesion (a) between the coated polystyrene particles and the rubber matrix and (b) between the uncoated polystyrene particles and the natural rubber matrix.

Functionalising the surfaces of polystyrene particles with allylmethacrylate units was also found to improve the ability of polystyrene particles to enhance tear strength, tensile strength and puncture strength of the film vulcanisates without any significant concomitant increase in stress at 300% extension. This suggests that rubber-filler bonding is a factor in reinforcement. That this is the case is also evident from the comparison between the mechanical properties, particularly tear strength and tensile strength, of vulcanisates containing these particles and vulcanisates containing polystyrene/polybutylacrylate core-shell particles. The latter particles were found not to enhance these properties. Since the only significant difference between the coating polymers is the presence of allylic double bond in the polyallylmethacrylate coat, the reinforcement manifested by the particles coated with polyallylmethacrylate is attributed to the formation of covalent chemical bonds between the rubber matrix and the particles surface. However, functionalising the surfaces of polystyrene particles with isoprene units appears not to improve the ability of polystyrene particles to reinforce. This is attributed to the presence of interlinkages between the molecules of the polyisoprene coating. These interlinkages would be expected to reduce the mixing interaction and possibly also the chemical

interaction (co-vulcanisation) between the particle coating and the rubber matrix.

It has also been found from experiments using the overcoated particles that optimum tear strength increases approximately linearly with increasing optimum tensile strength for the vulcanisates containing the various coated particles (see Figure 5.36, Section 5.16.2.). Overcoating polystyrene particles with acrylate polymers was found to reduce the unexpected increase in viscosity which has been observed on mixing polystyrene filler latices with natural rubber latex.

7.2.5 Effect of filler loading

Generally, it was found that with increasing loading of filler particles in the rubber, all the strength properties passed through a maximum for moderate loadings of fillers with the exception of stiffness which increases continuously. For each type of filler, optimum tear strengths were attained at loadings in the range 10 to 20 pphr.

7.2.6 Effect of milling; comparison between natural rubber vulcanisates loaded with polymeric filler and natural rubber vulcanisates loaded with carbon black

The tear strengths of films obtained directly from the blends of polystyrene latex or polymethylmethacrylate latex with natural rubber latex have been found to be superior to those of natural rubber vulcanisate sheets containing SAF black. However, the tear strengths of vulcanisate sheets prepared from the milled coagulum of the polymeric filler-rubber latex blends was found to be relatively lower than those of vulcanisate sheets containing carbon black, indicating that milling has an adverse effect upon the enhancement of tear strength by

rigid polymer particles. On the other hand, milling was found to increase the abilities of the polymeric filler particles to enhance the stress at 300% extension and puncture strength of the vulcanisate sheets. The effect upon tensile strength was not significant.

7.3 Conclusions concerning behaviour of polymeric filler particles in latex films derived from other rubber latices

7.3.1 Behaviour of added polymer particles in films from prevulcanised natural rubber latex

Experiments have been carried out with prevulcanised natural rubber latex using polystyrene particles overcoated with poly-dodecylacrylate, polyVeoVa 10 and polyallylmethacrylate. The core-shell particles were expected to give optimum reinforcement on the basis of the principles which had emerged from the experiments on post-vulcanised rubber latex films. It was found that the filler particles did not improve the tear strength of the film vulcanisates, in contrast to their effects upon post-vulcanised latex films. However, the filler particles were found to increase the stress at 300% extension and decrease the elongation at break as expected. No significant change was observed in the puncture strength. The filler particles appear to decrease the tensile strength. The observed effects of the filler particles upon tear strength of films derived from prevulcanised latex suggest that, in all cases investigated, the tearing of the prevulcanised films occurred by failure at the interface beteween the rubber particles, and that the presence of filler particles had little effect upon the process.

7.3.2 Behaviour of added polymer particles in films from styrene-butadiene rubber and acrylonitrile-butadiene rubber latices

Only initial exploratory work has been carried out in the present study concerning the behaviour of films from styrene-butadiene rubber and acrylonitrile-butadiene rubber latices. Polystyrene particles overcoated with polyVeoVa 10 were used in these exploratory experiments. Generally, the particles appear not to reinforce films from these latices.

7.4 Suggestions for further work

It has been confirmed during the course of this study that small particle size is a necessary prerequisite for the enhancement of optimum reinforcement in a filled polymer system. However, it has not been possible to prepare mono-dispersed filler particles having sizes below 50nm. Therefore it would be interesting to attempt to prepare mono-dispersed particles having sizes well below 50nm say 20 to 30nm (i.e., similar to SAF black). One could then investigate the effects of these very small filler particles, and also of the nature of their surfaces, upon the reinforcement of films derived from rubber latices.

It may be desirable to repeat much of the work described here using a peroxide vulcanisation system instead of sulphur vulcanisation system, particularly in natural rubber containing overcoated polystyrene particles. Peroxides such as dicumyl peroxide function by thermal rupture into free radicals, which in turn will remove active hydrogen atoms from rubber molecules. These then crosslink by combination of the free radicals one with another. The radicals yielded by peroxide are very reactive, and will abstract hydrogen atoms from any available source. Therefore in a system comprising natural rubber and say, polystyrene/polyallylmethacrylate core-

shell particles which is undergoing peroxide vulcanisation, it is to be expected that hydrogen atoms will also be abstracted from the polyallylmethacrylate molecules. The resulting radicals will presumably combine with rubber radicals to form polystyrene/polyallylmethacrylate-rubber covalent chemical linkages. Such chemical linkages might infuence the mechanical properties of the filled films produced by this system.

It would also be of considerable interest to carry out further investigations of the behaviour of polymer particles in films derived from prevulcanised natural rubber latex, with the aim of preventing failure at the interface between the rubber particles. In the present work, the inability of polymeric filler particles to enhance the tear strength of prevulcanised natural rubber latex films has been attributed to tearing of the films occurring by failure at the interface between the rubber particles, and that the presence of the filler particles had little effect upon the process. Similarly, other workers (1) have attempted to use polymer particles, such as polystyrene particles and various vinyl copolymers and terpolymers, to obtain improvements in the tear strength of prevulcanised natural rubber films, and have found no improvement in the tear strength. However, the same workers have reported that addition of polyvinylchloride (PVC)(7.5 pphr) to prevulcanised natural rubber enhanced the tear strength marginally. In this connection, it would be interesting to prepare core-shell particles consisting of a polystyrene inner core and a polyvinylchloride outer shell. The behaviour of the core-shell particles could then be studied in films derived from prevulcanised natural rubber latex, and possibly also in post-vulcanised natural rubber latex films for comparison.

As already stated, only initial exploratory work has been carried out in the present work concerning the behaviour of polymer particles in films derived from rubber latices other than natural rubber latex. It would therefore be interesting to study this aspect of the

subject in greater detail in order to establish whether the principles which have emerged from the experiments on post-vulcanised natural rubber latex films are applicable to other polymer systems.

APPENDIX A : CALCULATION OF THE AMOUNT OF MONOMER AND SOAP REQUIRED FOR SEEDED EMULSION POLYMERISTION

(I) Calculation of the amount of monomer to be added to a seed latex in seeded emulsion polymerisation

Let D_1 be the average diameter of the seed latex particles, D_2 be the average diameter of the particles in the product of the second step of the seeded emulsion polymerisation, V_1 be the volume of the seed latex particles and V_2 be the volume of the final latex particles. Then

$$V_1 = \pi D^3/6 \quad \text{and} \quad V_2 = \pi D^3/6$$
$$V_1/V_2 = (D_1/D_2)^3 \qquad \text{A.1}$$

As the densities of the seed latex particles and the final latex particles are the same, equation A.1 becomes

$$W_1/W_2 = (D_1/D_2)^3 \qquad \text{A.2}$$

where W_1 and W_2 are the weights of the seed latex particles and the final latex particles respectively.

Therefore, if one requires to double the size of the seed latex particles, i.e., $D_2/D_1 = 2$, equation A.2 shows that an amount of monomer equal to seven times the weight of the seed latex particles has to be added to the seed latex.

(II) Calculation of the amount of soap to be added to a seed latex in the emulsion polymerisation

If D_2 is expressed in nm, ρ is the density of the polymer in Mgm^{-3}, then the number of particles, N, which comprises Wg of polymer is

$$N = \frac{6W}{\pi \rho D^3} \times 10^{21} \quad \text{particles}$$

The surface area, S, of Wg of particles is

$$S = \frac{6W}{\rho D_2} \times 10^{21} \quad (nm)^2$$

If A is the molcular adsorption area of soap on the polymer expressed in $(nm)^2 molecule^{-1}$, then for 100% soap coverage, Wg of polymer will require

$$= \frac{6W}{\rho D_2 A} \times 10^{21} \quad \text{molecules of soap}$$

$$= \frac{6W}{\rho D_2 A N_A} \times 10^{21} \quad \text{moles of soap}$$

where N_A is Avogadros' number. Therefore, for 50% soap coverage, the amount of soap required by Wg of the polymer will be

$$= \frac{3W}{\rho D_2 A N_A} \times 10^{21} \quad \text{moles}$$

APPENDIX B : STATISTICAL EVALUATION OF RELIABILITY

The statistical confidence limits for the mean, $\bar{x}$, of the measured values, x, were derived by calculating the sample standard deviation, σ, and the standard error of the mean SE(mean). This was done by using the following equations and the values of t given in standard statistical tables (1).

$$\bar{x} = \frac{\Sigma x}{n} \qquad \text{B.1}$$

$$\sigma = \left[\frac{\Sigma x^2}{n} - \bar{x}^2 \right]^{1/2} \qquad \text{B.2}$$

$$SE(mean) = \frac{\sigma}{(n-1)^{1/2}} \qquad \text{B.3}$$

$$\text{confidence limit} = \pm t SE(mean) \qquad \text{B.4}$$

where n is the number of measured values.

Example of calculation

The tear strength values of 12 test-pieces of films derived from natural rubber latex reinforced with polystyrene latex particles (10 pphr) were as follows (units: kNm^{-1}) :

183, 187, 136, 166, 165, 162
173, 163, 150, 145, 166, 152

then

$\bar{x} = 162\ kNm^{-1}$

$= 14.2\ kNm^{-1}$

$SE(mean) = 4.28\ kNm^{-1}$

The "double sided" value of t for n = 11 at the 5 percent significance level (i.e., the value which will fall within the range specified in 95 out of every 100 cases) is 2.20. Thus for equation B.4

$$\text{confidence limits} = \pm 9.42 \text{ kNm}^{-1}$$

Thus the value of the mean 162 kNm^{-1} can be quoted as 162 $\pm$ 9 kNm^{-1}

APPENDIX C1 : PROGRAM FOR t-TEST

```
10 REM *** TEST OF SIGNIFICANCE FOR SMALL (N<30) SAMPLES **
20 REM     variables  N1 - no of data in sample one        '
                      N2 - no of data in sample two        '
                      X1 - mean of sample one              '
                      X2 - mean of sample two              '
                      S1 - standard deviation of sample one'
                      S2 - standard deviation of sample two'
                      T  - value of t
30  REM ************* INPUT YOUR DATA *********
40  PRINT
50  PRINT
60  PRINT "NUMBER OF DATA IN SAMPLE ONE"
70  INPUT N1
80  PRINT "MEAN OF SAMPLE ONE"
90  INPUT X1
100 PRINT "STANDARD DEVIATION OF SAMPLE ONE"
110 INPUT S1
120 PRINT "NUMBER OF DATA IN SAMPLE TWO"
130 INPUT N2
140 PRINT "MEAN OF SAMPLE TWO"
150 INPUT X2
160 PRINT "STANDARD DEVIATION OF SAMPLE TWO"
170 INPUT S2
180 REM ************* CALCULATION **************
190 LET A = N1 * S1 * S1
200 LET B = N2 * S2 * S2
210 LET C = N1 + N2 - 2                    !degree of freedom
220 LET D = ((A+B)/C) ** 0.5               !weighted std.dev.
230 LET E =  X1 - X2
240 LET F = (1/N1 + 1/N2) ** 0.5
250 LET T = INT((E/(D*F)*100+0.5)/100      !t-value to dec.
260 REM ************* RESULTS ******************
270 PRINT
280 PRINT
290 PRINT "T VALUE = "; T
```

```
300 REM ****************************************
310 PRINT
320 PRINT
330 PRINT "MORE CALCULATION ? TYPE Y FOR YES AND N FOR NO
340 INPUT A$
350 IF A$ = "Y" THEN GOTO 30
360 IF NOT ( A$ = "N" ) THEN 300
370 REM ************ END OF PROGRAM **********
380 PRINT
390 PRINT
400 PRINT "BYE FOR NOW"
410 PRINT
420 PRINT
430 END
```

APPENDIX C2 : PROGRAM FOR PAIRED COMPARISON t-TEST

```
10 REM **PAIRED COMPARISON t-TEST FOR SMALL (N<30)SAMPLES*
20 REM      variables  N = number of data (paired)          '
                       A = data in sample one              '
                       B = data in sample two              '
                       C = paired difference               '
                       T = value of t                      '
30  REM ************** INPUT YOUR DATA *****************
40  PRINT "NUMBER OF DATA (PAIRED)"
50  INPUT N
60  DIM A(N), B(N), C(N)
70  PRINT
80  PRINT "INPUT DATA IN FORM A,B" .
90  REM ************ INPUTED DATA STORED ***************
100 FOR I = 1 to N
110 INPUT A(I), B(I)
120 NEXT I
130 PRINT
140 PRINT "NO", " A", " B", " C"
150 REM ****** DIFFERENCE IN PAIRED DATA STORED ******
160 FOR I = 1 TO N
170 LET C = A(I) - B(I)
180 LET A = A(I)
190 LET B = B(I)
200 PRINT I, A, B, C
210 NEXT I
220 REM ****** DIFFERENCE IN PAIRED DATA ADDED *******
230 LET C = 0
240 FOR I = 1 TO N
250 LET C = C + A(I) - B(I)
260 NEXT I
270 REM * CALCULATION OF t-VALUE FOR THE PAIRED DATA *
280 LET C = C * (N-1) ** 0.5
290 LET T = INT(C*100+0.5)/100        !t corrected to 2 dec.
300 REM ******************** RESULTS *******************
310 PRINT
```

```
320 PRINT " T value  =; t
330 REM ****************************************
340 PRINT
350 PRINT
360 PRINT "MORE CALCULATION ? TYPE Y FOR YES AND N FOR NO
370 INPUT A$
380 IF A$ = "Y" THEN GOTO 30
390 IF NOT ( A$ = "N" ) THEN 330
400 REM ************ END OF PROGRAM **********
410 PRINT
420 PRINT
430 PRINT "BYE FOR NOW"
440 PRINT
450 PRINT
460 END
```

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CHAPTER 7

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APPENDIX B

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TITLE

MECHANICAL REINFORCEMENT OF FILMS FROM RUBBER LATICES BY ADDED POLYMER PARTICLES

AUTHOR

Kolapo Albert Popoola,

INSTITUTION and DATE

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